İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECTS OF ANIONIC SURFACTANTS ON STYRENE-ACRYLIC COPOLYMER EMULSION FOR WOOD COATINGS

M.Sc. THESIS

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Department of Polymer Science and Technology

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Thesis Advisor: Prof. Dr. İ.Ersin SERHATLI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AHŞAP KAPLAMALARDA ANYONİK SÜRFAKTANLARIN STİREN-AKRİLİK EMÜLSİYONLAR ÜZERİNE ETKİSİ

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HAZİRAN 2016

Gülşah UZUN, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515071026, successfully defended the thesis entitled "Effects of Anionic Surfactants in Styrene-Acrylic Copolymer Emulsion for wood coatings", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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FOREWORD

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And special thanks to my mom, dad and my husband for their love and support.

May 2016

Gülşah UZUN
Chemist

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ABBREVIATIONS

^{1}H-NMR	**:** Proton Nuclear Magnetic Resonance
1,3-BDDMA	**:** 1,3-Butanediol Dimethacrylate
1K	**:** One Component
2K	**:** Two Component
APEO	**:** Alkylphenol Ethoxylate
BA	**:** Bultyl Acrylate
CMC	**:** Critical Micelle Concentration
DIY	**:** Do it yourself
EO	**:** Ethylene Oxide
HLB	**:** Hydrophilic-lipophilic Balance
MFFT	**:** Minimum Film Forming Temperature
MMA	**:** Methyl Methacrylate
NPEO	**:** Nonylphenol Ethoxylate
SEM	**:** Scanning Electrone Microscope
Sty	**:** Styrene
***t*-BHP**	**:** Tertiary Butanedioldimethacrylate
T_g	**:** Glass Transition Temperature
UV	**:** Ultraviolet
VAc	**:** Vinyl Acetate
VOC	**:** Volatile Organic Content

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EFFECTS OF ANIONIC SURFACTANTS ON STYRENE-ACRYLIC COPOLYMER EMULSION FOR WOOD COATINGS

SUMMARY

Wood coatings have the biggest share in industrial coatings market. Because of high VOC content of conventional solvent-based systems, the market share of low-VOC systems are increasing year by year. Low-VOC systems are water-based, UV curable and high solid systems. For economic reasons, water-based low-VOC coating systems are getting more popular. Because of the low cost and ease of application of water-based 1K acrylic emulsion systems, they have the biggest increase within low-VOC systems.

Water-based 1K acrylic systems differentiate in terms of their end use application and application method. It is convenient for brush, spray, curtain or roller coater systems. In terms of end use, both opaque and clear paints can be formulated with 1K acrylic systems. It has a wide range of application like furniture, exterior wood substrates, floors, industrial mdf panels, etc.

From chemical point of view, styrene-acrylic copolymers, pure acrylic copolymers or vinyl acrylic copolymers can be used in several wood coating application.

Main performance criterias are hardness, early hardness development, sandability of the film, scratching resistance, drying time, blocking resistance, chemical resistance and asthetistical properties.

The aim of this study is to examine how a range of different anionic surfactants affect the polymerization of styrene-acrylic emulsion and the end properties of an interior clear wood coating system prepared with these copolymers.

The surfactants used in this study include different types of anionic surfactants as sodium lauryl suphate, sodium lauryl ether sulphate (2EO and 4EO), sodium dodecylbenzene sulphonate, alkyl polyethylene glycol ether sulphate, polyoxyhethylene tridceyl phospate ester and disodium exthoxylated alcohol [C_{10}-C_{12}] half ester of sulfosuccinic acid.

For the sake of uniform conditions, the same recipe is used for polymerization except surfactant. Seven latexes were prepared as binders for interior clear wood coating. Particle size distribution of the copolymers are measured to check the effect of anionic surfactants.

Seven clear wood topcoat formulation prepared with the same fomulation except copolymer as the binder. Formed films prepared from clear wood topcoat formulation were tested for gloss, hardness, coin resistance, chemical resistance and blocking. The best performing topcoat formulation is selected and the sulphur containing silane VTET added in three different ratio as 0,1 %, 0,5 % and 1 %. The effect of VTET is also tested in terms of gloss, hardness, coin resistance, blocking and hydrophobic charachter of the film.

AHŞAP KAPLAMALARDA ANYONİK SÜRFAKTANLARIN STİREN-AKRİLİK EMÜLSİYONLAR ÜZERİNE ETKİSİ

ÖZET

Ahşap kaplamalar, endüstriyel kaplama uygulamalarında en büyük paya sahiptir. Konvansiyonel solvent bazlı ahşap kaplamalar, yüksek uçucu organik bileşik içerikleri sebebiyle insan sağlığını tehdit etmeye devam ediyor. Regülasyonlarla düşük uçucu organik bileşikler içeren kaplama sistemleri yaygınlaştırılmaya çalışılıyor. Bu sistemler, 1K ve 2K su bazlı sistemler, UV kürlenmeli sistemler ve yüksek katılı sistemler ana başlıkları altında incelenmektedir.

Düşük uçucu bileşik içeren sistemler arasında, düşük yatırım maliyeti ve uygulama kolaylığı sebebiyle son yıllarda popülerliği en çok artan sistem 1K su bazlı sistemler olmuştur. Bunların arasında da maliyeti en düşük olan 1K su bazlı akrilik sistemlerdir. Bu sistemler genel olarak stiren-akrilik kopolimerler, saf akrilik kopolimerler ve vinil akrilik kopolimerlerdir.

1K su bazlı akrilik kopolimer sistemlerinin uygulama şekilleri çok geniştir. Endüstride fırça, rulo, sprey, merdane veya perde uygulama gibi çok çeşitli yöntemlerle uygulanabilmektedirler. Uygulama alanları da benzer şekilde çok çeşitlidir. Mobilya, dış mekan ahşaplar, ahşap dış cephe kaplamalar, ahşap yapılar, zemin ve parkeler, endüstriyel mdf kaplamaları gibi çok çeşitli uygulama alanına sahiptir.

1K su bazlı akrilik kopolimerler emülsiyon polimerizasyonu metoduyla üretilmektedir. Emülsiyon polimerizasyonu metodundaki ana girdiler, monomerler, başlatıcılar, sürfaktanlar ve sonlandırıcı, çarpraz bağlayıcı gibi diğer kimyasallardır. Emülsiyon polimerizasyonunda monomer kompozisyonu, kopolimerin ana özelliklerini verir. Fakat, polimerizasyon sürfaktanların oluşturduğu misel içerisinde gerçekleştiği için sürfaktanların kopolimer özellikleri üzerindeki etkileri büyüktür.

Bu çalışmada, farklı anyomik karakterdeki sürfaktanların, stiren, butil akrilat ve metilmetakrilat monomer kompozisyonuna sahip kopolimer üzerindeki etkileri incelenmiştir. Çalışmada, sodyum lauril sülfat, sodyum lauril eter sülfat (2EO ve 4EO), sodyum dodecilbenzen sülfonate, alkil polietilen glikol eter sülfat, polioksietilen tridecil fosfat ester ve sülfosüksinik asidin disodyum etoksile alkol [C_{10}-C_{12}] yarı esteri olmak üzere 7 farklı anyonik yapıda sürfaktan kullanılmıştır.

Tüm kopolimerler, sadece sürfaktan değiştirilmek kaydıyla aynı formül ve proses ile hazırlanmıştr. Hazırlanan kopolimerlerin partikül boyutu dağılımı ölçülmüş ve sürfaktan karakteri ile partikül boyutu dağılımı arasındaki bağlantı incelenmiştir. Akabinde ahşap kaplamalar üzerindeki etkisini incelemek amacıyla tüm kopolimerler ile ayrı ayrı, sadece kopolimer değiştirlmek kaydıyla, aynı formül kullanılarak 1K su bazlı iç mekan mobilya sonkat vernik hazırlanmıştır. Hazırlanan vernikler kayın kaplı mdf üzerine havalı sprey tabanca ile uygulanarak, sertlik, çizilme direnci, parlaklık, kimyasal direnç, bloklanma direnci gibi nihai kaplama performansları karşılaştırılmıştır. Burada amaç, kullanılan farklı anyonik sürfaktanların kopolimer yapısı üzerindeki etkilerini incelerken, iç mekan mobilya sonkat verniğin nihai performansı üzerindeki etkisini de incelemek.

Hazırlanan 7 vernik arasında en iyi performans gösteren vernik, dolayısıyla kopolimer seçilerek, bu kopolimer ile ayrıca vernik hazırlanmış ve sülfür içeren silan katkı VTET, farklı oranlarda eklenerek silanın performans üzerindeki etkisi araştırılmıştır. Çalışmada VTET % 0,1, % 0,5 ve % 1 oranlarında vernik formülasyonuna eklenerek kayın kaplı mdf üzerine ve cam üzerine uygulanmış, parlaklık, yapışma, hidrofobisite özelliklerindeki değişim incelenmiştir.

1. INTRODUCTION

There is a movement in the wood coatings industry to reduce the use of solvent-borne coatings, which have a high volatile organic compound (VOC) content [1]. Switching to low- or no-VOC coatings would both reduce environmental pollution and increase the volume of wood that can be coated. Thus, there has been a great deal of research focused on replacements for solvent-borne wood coatings [2–9].

Because water-borne coatings are able to combine low solids with a low VOC, they can be formulated to undergo considerable shrinkage on drying. This is beneficial if open-pore effects are required, and also to allow the effective use of matting aids where a satin or low gloss is required. However, water is unique among solvents for its affinity to biological systems and its prevalence in the atmosphere, resulting in some specific differences from non-aqueous solvents. Among these must be numbered grain-raising and drying issues.

All species of wood will absorb moisture as liquid or vapour but the effect on grain-raising is very species dependent. Oak (Quercus robur), for example, can show severe grain-raising whereas Pine (Pinus sylvestris) is much less prone. Veneers are generally less affected than the solid wood.

The appearance and properties of water-borne coatings will depend very much on the specific chemistry chosen. Often, the polymers used in used in water-borne dispersions will have a lower refractive index than solvent-borne polymers, and this possibly combined with a degree of incomplete coalescence gives a translucent effect especially on dark substrates. For this reason, water-borne finishes are more suited to low-build finishes on light coloured timbers. Another coloration effect arises from the fact that water-borne lacquers are almost invariably high in pH (i.e. alkaline) and can produce a significantly different colour from acidcatalysed products either initially or over a period of time. Some waterborne coatings contain amines which have specific coloration effects with certain woods.

The appearance of clear coatings on wood is sometimes described by the subjective term ‘Anfeuerung’. It relates to the enhancement of wood appearance in terms of grain contrast, warmth and lack of haze. Generally a ‘good’ Anfeuerung is harder to achieve

with water-borne systems, but the effect is system specific and will depend upon the refractive index of the polymers in the coating, and also particle size in the case of dispersion systems.

In terms of dry film properties, water-borne acrylic coatings are thermoplastic and borderline for durability tests such as marking by liquids and wet heat. This can be improved upon by cross-linking variants [10].

Water-borne one-component acrylic systems have grown in popularity with furniture paint applicators in recent years because of their ease of use and good cost profile. A key factor in this growth has been the increased performance of water-borne acrylic systems, in particular hardness development and improvements in early block resistance.

One major area where further performance improvements are required is in chemical resistance, particularly in respect of solvents and highly staining chemicals. For a long time this could only be achieved with two-component or UV cross-linkable systems.

A new generation of 1K resins in a well-designed formulation now makes it possible to obtain coatings with improved chemical resistance to alcohol and coffee, even in pigmented systems. Good hardness development and early block resistance, needed for industrial coating application line speeds, are also maintained [11].

Surfactants are commonly used during emulsion polymerization to produce stable dispersions of polymer particles for applications such as paints, adhesives and other coating applications. Surfactants can improve properties such as shelf-life, freeze–thaw stability and mechanical stability. However, the addition of surfactants can also have a negative effect on end-use properties, such as the water resistance of the coating. The type and amount of surfactant used is an important determinant of system behaviour during polymerization, film formation, and throughout the lifetime of the formed coating.

The molecular architecture of binder particles is of crucial importance to latex paint properties. The type of surfactant used to stabilize binder particles had an effect on the adhesion of the paint.

Surfactants are commonly used during emulsion polymerization to produce latexes, stable dispersions of polymer particles in an aqueous environment [12]. The latexes produced from this process are used in applications such as adhesives, paints, and other coating applications. In these applications, the prevention of sedimentation and phase separation during the manufacture and storage of the particles is desirable. The use of

surfactants improves latex properties such as shelflife stability, freeze–thaw stability and mechanical stability.

However, the addition of surfactants can have a negative effect on film properties such as the water resistance of the coating [13,14].

Thousands of different commercial surfactants are available for use in emulsion polymerization. The type used will determine the behaviour of the system during polymerization, during film formation, and under end-use conditions [15].

Nonylphenol ethoxylates (NPEOs) are widely used as surfactants for emulsion polymerization and for post adding stabilization for latex applications in formulations with high filler content. However, NPEOs are bioaccumulative and persistent in the environment while nonylphenol, the breakdown product of NPEs, is an endocrine disruptor. Therefore, the EU Commission has recommended implementing a risk reduction strategy, which foresees the ban of all applications leading to direct emissions to waste water and strict emission controls for all other technical processes using NPEOs as surfactants [16].

2. THEORETICAL PART

2.1 Emulsion Polymerization

Emulsion polymerization is an important technical procedure for the preparation of polymers on any scale and by any method. It has attracted industrial and academic researchers for almost a century. The main driving force in the late 19th and early 20th centuries was an attempt to copy natural rubber (cis-polyisoprene) and to find a synthetic route to rubber polymers [17–19]. The cradle of emulsion polymerization was in Leverkusen, where Kurt Gottlob in 1912 invented a process for the preparation of synthetic rubber by polymerization of isoprene in aqueous viscous solutions [20]. He used egg albumen, starch or gelatin as stabilizers and he noticed that the addition of alkali or organic bases led to an improvement of latex stability. At the end of the polymerization, coagulation was possible by lowering the pH. The polymerization was started only thermally and hence took a period of up to several weeks. For example, 7 g of egg albumen were placed with 500 g of water and 300 cm^3 of isoprene in an autoclave and stirred at 60°C. Another patent, filed shortly afterwards, also claimed the use of blood serum and cow's milk as stabilizers [21]. There was significant progress in the development of the emulsion polymerization technique during the following decades, when the above natural stabilizers were replaced by oleates or alkyl aryl sulfonates, and when water and monomer soluble peroxides were employed, which allow a faster and more controlled polymerization process [22–24]. The development of emulsion polymerization has now reached the point at which it is an important economic factor in the overall polymer business. The 8×10^6 metric tonnes of polymers (dry) that are sold worldwide and applied as latexes (frequently called emulsion polymers) represent a value of more than 20 billion [25]. Note that the overall amount of polymers produced by emulsion polymerization is almost twice as high, because many polymers, such as poly(vinyl chloride) and synthetic rubber, are sold and applied as bulk material but prepared via emulsion polymerization. Additionally, about 7×10^6 metric tonnes of natural rubber are produced yearly on plantations in South-East Asia, and this is expected to increase [26]. When classified by monomer base, about 37% of emulsion polymers are styrene-butadiene copolymers, 30% are

acrylic- or methacrylic-based (co)polymers and 28% are vinyl acetate-based (co)polymers, leaving 5% others. The main application areas for emulsion polymers are paints and coating (26%), paper/paperboard (23%), adhesives (22%), carpets (11%) and miscellaneous (18%) [27].

From a more scientific point of classification, emulsion polymerization belongs to the class of heterophase polymerizations, which includes suspension, microsuspension, miniemulsion, microemulsion, dispersion and precipitation polymerizations. All these techniques, which lead to various kinds of polymer dispersion, are characterized by their heterogeneous nature [28].

Emulsion polymerization is a heterogeneous polymerization technique in which the polymer is synthesized from water insoluble monomers in the form of particles suspended in water. Though reverse processes are also developed in which the water soluble monomers are polymerized in organic solvents, these processes are not as common as conventional emulsion polymerization. In the emulsion polymerization, the monomers, e.g., styrene, methyl methacrylate, etc., are suspended in water in which a surfactant has been added [29].

2.1.1 Ingredients of emulsion polymerization

A laboratory scale recipe for an emulsion polymerization contains monomer, water, initiator, surfactant, and sometimes a buffer and/or chain transfer agents. Commercial emulsion polymerization recipes are usually much more complicated, with 20 or more ingredients. The complexity of components, and the sensitivity of the system kinetics, mean that small changes in recipe or reaction conditions often result in unacceptable changes in the quality of the product formed [30].

2.1.1.1 Monomers

Particles in an emulsion polymerization comprise largely monomers with a limited solubility in water. The most common monomers are styrene, butadiene, vinyl acetate, acrylates and methacrylates, acrylic acid and vinyl chloride. Besides monomers that make up a large part of the latex, other monomers are often added in smaller quantities and have specific functions, like stabilization ((meth)acrylic acid) and reactivity in crosslinking (epoxy-group containing monomers, amine- or hydroxy functional groups etc.). These are often denoted “functional monomers” [30].

2.1.1.2 Initiators

The initiator for emulsion polymerization has to be water-soluble, considering the mechanism of emulsion polymerization.

Typical initiators are persulfates, for example, sodium, potassium, or ammonium persulfate, which are activated by thermal energy; typical polymerization temperatures are in the range of 70–90 °C.

Very popular are also redox systems, which consist of an oxidizing and a reducing compound. The interaction of these components and optionally some multivalent metal ions generates radicals even at low temperatures and allows smooth polymerization.

The best-known redox initiators are based on Fe(II) and peroxides:

$$H_2O_2 + Fe^{2+} \rightarrow HO + HO^- + Fe^{3+}$$

Instead of the water-soluble hydrogen peroxide, oil-soluble organic hydroperoxides and sparingly soluble Fe(II) salts or complexes are used in order to reduce the concentration of reactants in the aqueous phase and proceed to a uniform rate of radical-formation. Reducing sugars may be used to convert the Fe(III) which is formed, back to Fe(II)

Another well-known redox system is peroxodisulfate–bisulfite: [31]

$$S_2O_8^{2-} + HSO^{3-} \rightarrow SO_4^{2-} + OSO_3^- + OSO_2H$$

In cases where the polymerization should be performed at lower temperatures (less than 50°C), a redox system can be used. Lower polymerization temperature gives the advantage of lowering chain branching and crosslinking in the synthesis of rubbers. Usually the redox couple reacts quickly to produce radicals, and thus one or both components must be fed during the course of the emulsion polymerization process. For this reason, redox initiators are very useful for safety in commercial emulsion polymerizations because, in the case of a threatened thermal runaway (uncontrolled exotherm), the reaction can be quickly slowed by switching off the initiator feed. A typical example of a redox system is tert- butyl hydroperoxide and sodium metabisulfite. While reductants such as Fe^{2+} can be used, these tend to produce discoloration and also may induce coagulation of the latex particles.

There are also other methods to create free radicals, such as γ-radiolysis, light in combination with photoinitiators, and electrons from high energy electron beams. One of the advantages is that these alternative methods can produce pulses of radicals and in this way an influence on the growth time of the polymer can be obtained. On the laboratory scale these methods are used to obtain kinetic parameters [30].

2.1.1.3 Surfactants

A surfactant (surface active agent), also referred to as emulsifier, soap or stabilizer, is a molecule having both hydrophilic and hydrophobic segments. The general name for this group is amphipathic, indicating the molecules' tendency to arrange themselves at oil/water interfaces. In emulsion polymerization surfactants serve three important purposes: stabilization of the monomer droplets, generation of micelles, and stabilization of the growing polymer particles leading to a stable end product [30].

2.1.1.4 Other ingredients

Electrolytes:

Electrolytes are added for several reasons. For example, they can control the pH (buffers), which prevents hydrolysis of the surfactant and maintains the efficiency of the initiator. The addition of electrolytes can lead to more monodisperse particles but also to coagulation.

Chain Transfer Agents:

Emulsion polymerization may result in an impractically high molecular mass polymer. To reduce the molar mass, chain transfer agents (CTA), usually mercaptans, are frequently used. The mercaptan is introduced into the reactor together with the monomer phase. The consumption of the mercaptan taking place in the location should be properly kept in balance with monomer consumption.

Sequestering agents:

In redox systems, adventitious metal ions can catalyse radical formation in an uncontrolled way. So-called sequestering agents (for example EDTA) are added to prevent this [30].

2.1.2 Mechanism of emulsion polymerization

Emulsion polymerization is a type of free-radical polymerization. In emulsion polymerization, monomer mixtures are dispersed in water with the aid of suitable emulsifiers. The polymerization reaction, which takes place at elevated temperatures, is initiated by water-soluble initiators and occurs in micelles.

Emulsion polymerization is carried out in water using monomers, surfactants (emulsified) and a water soluble initiator. As shown on the Figure 2.1. the monomers are emulsified in water with surfactant molecules oriented at the surface of the emulsion droplets, stabilizing the emulsion. There is also surfactants dissolve in the water and excess surfactant present in micelles. This polymerization is a chain reaction initiated by the decomposition of an initiator molecule. This initiator radicals attack the double bond of monomer and forming chain radicals. These radicals react with a further monomer molecule to produce extended chain radicals. The chain reaction continues to propagate until the growth of the chains is terminated by recombination or disproportion [32-33].

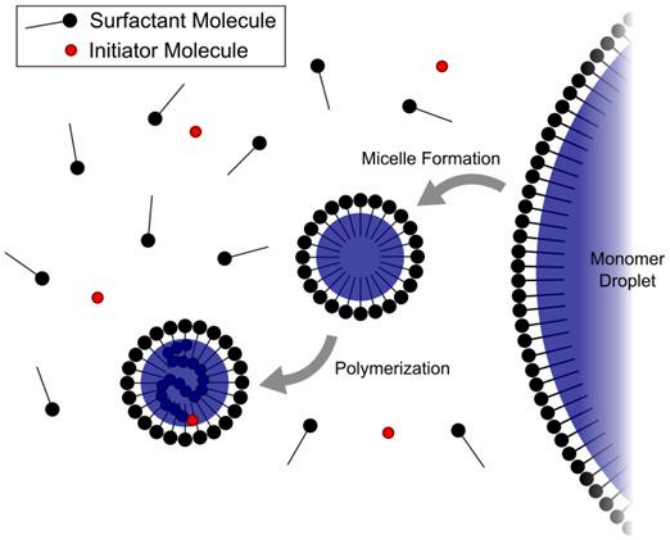


Figure 2.1 : Mechanism of emulsion polymerization.

The emulsifier concentration in the continuous aqueous phase at the beginning of emulsion polymerization is above the critical micelle concentration (CMC), and thus micelles form. The hydrophobic interior of the micelles contains solubilized monomers, which migrate by diffusion out of the emulsified monomer droplets and through the aqueous phase. The water-soluble initiator decomposes in the water phase to generate primary radicals, which react with the monomer dissolved in water to form

oligomeric radicals with surface-active properties. When such a surface-active oligomeric radical enters a micelle, it propagates rapidly with the solubilized monomer to form a polymer particle. In a typical emulsion polymerization, there are about 10^{13} monomer droplets per liter of emulsion, with an average droplet size of about 103 nm. This compares with ~10^{18} micelles with a diameter of about ~5 nm. The total interfacial area of the micelles is about 3 orders of magnitude larger than that of the monomer droplets (Figure 2.2). Consequently, oligomeric radicals in the aqueous phase are much more likely to diffuse into a micelle swollen with monomer than into a monomer droplet. Polymerization thus occurs almost exclusively in the micelles and in the polymer particles which are later formed, consuming monomer that arrives by diffusion through the aqueous phase from the monomer droplets.

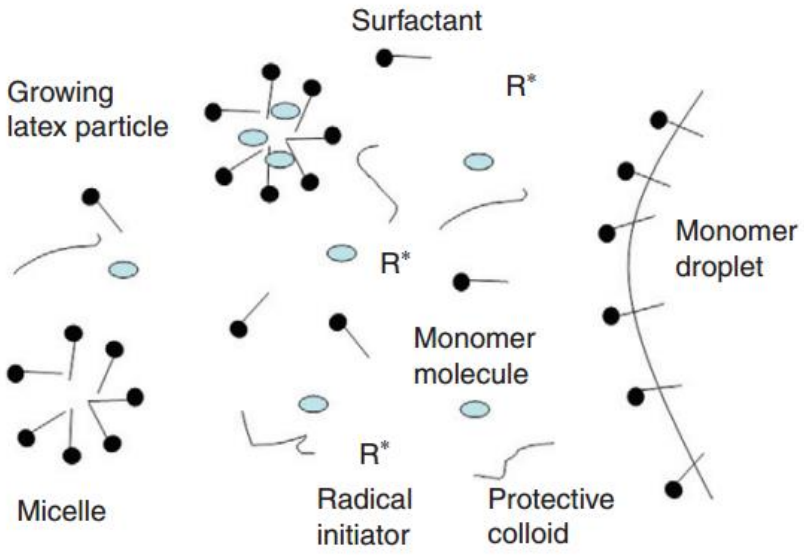


Figure 2.2 : Scheme of emulsion polymerization.

One big advantage of the process is that nearly no waste materials are connected with the production of aqueous emulsions. All materials used in the process are included in the final product. The only wastes are some filtration residues and the monomer-contaminated process water (e.g., pumps). Also process emissions are very low due to the fact that residual monomer stays in the final product most of the time.

However, residual monomer in the final product has initiated an increasing demand for reducing the VOC in the final consumer product [31].

Emulsion polymerization is a particularly attractive route for the production and control of polymer structures on a size scale from a few hundred nanometers to several

microns. This section is then the first instance in this text in which polymerization reactions are considered on a scale larger than molecular.

The essential ingredients in an emulsion polymerization are the water, a monomer which is not miscible with water, an oil-in-water emulsifier, and a compound or compounds that release free radicals in the aqueous phase. Other ingredients which may be used in practical recipes are mentioned briefly later. Typical proportions (by weight) are monomers 100, water 150, emulsifier 2-5, and initiator 0.5, although these ratios may vary over a wide range.

Figure 2.3 is a schematic of a typical laboratory apparatus for emulsion polymerization. Industrial reactors are usually large-scale versions of this basic arrangement, with the modifications that the reactor will have a bottom discharge valve and a jacket for temperature control [34].

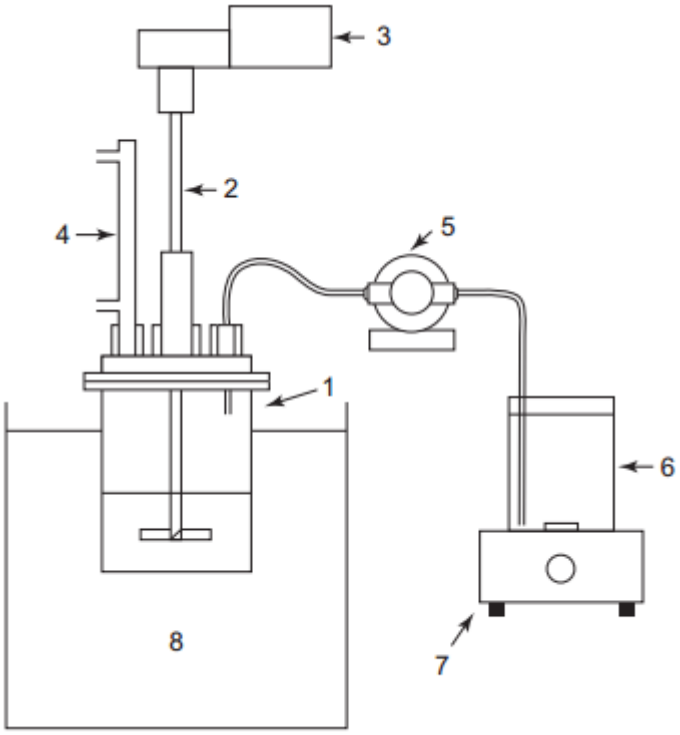


Figure 2.3 : Laboratory emulsion polymerization apparatus. 1, reactor; 2, stirrer; 3, motor; 4, reflux condenser; 5, pump; 6, monomer feed; 7, magnetic stirrer; 8, water bath.

2.1.3 Acrylic emulsion polymerization

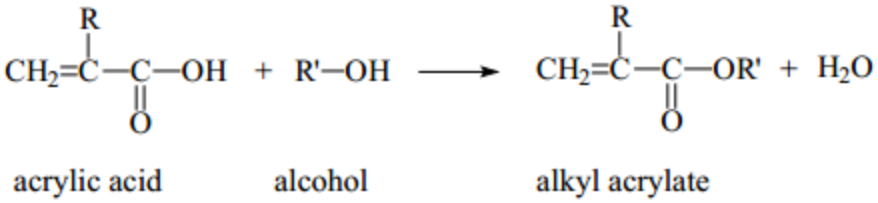
Since their introduction decades ago, acrylic polymers have gained a strong foothold in the coatings and allied industries as a result of their improved flexibility and adhesion compared to polyvinyl acetate emulsions, phenolics, and styrene-butadiene

latex combined with their moderate cost. In addition, their significantly improved outdoor durability, including resistance to ultraviolet degradation, has mandated their use in several applications. In many respects, the name “acrylic” has become synonymous with a high performance level in a polymer system.

Presently, acrylics are available in three physical forms: solid beads, solution polymers, and emulsions. The emulsion form is by far the dominant form in use today. This is due generally to the ease of tailoring properties, and the lower hazards and manufacturing costs compared to the solid and solution polymers.

Acrylic monomers are esters of acrylic and methacrylic acid. Some common esters are methyl, ethyl, isobutyl, n-butyl, 2-ethylhexyl, octyl, lauryl, and stearyl. The esters can contain functional groups such as hydroxyl groups (e.g., hydroxyethyl methacrylate), amino groups (e.g., dimethylaminoethyl methacrylate), amide groups (acrylamide), and so on, in addition to the carboxylic acid functionality of the unesterified monomer. Acrylic monomers can be multifunctional (e.g., trimethylolpropane triacrylate, or butylenes glycol diacrylate, to mention two). The polymer chemist has a wide range of monomers to select from when designing a specialty polymer system [35].

Monomers, are prepared by a reversible reaction between an acrylic acid and an alcohol as shown below:



The major monomers used are ethyl acrylate, methyl methacrylate and butyl acrylate, as well as non-acrylic monomers such as vinyl acetate and styrene which behave similarly. Homopolymers latexes of these monomers have wide range of application areas such as paint, coating, textile, leather, construction etc. These polymers are stable, have good pigment binding capacity, durability, chemical resistance, impact resistance. Wide range of copolymers can be produced, and by varying the ratio of their monomers a series of polymers with a wide range of glass transition temperatures can be produced with emulsion polymerization method [33,36,37].

Water, is used as the medium to disperse and wet the micelles. During the emulsion polymerization process the water acts as a solvent for the surfactants and initiators, as well as a heat transfer medium [37,38].

The initiators (catalysts), usually used are water soluble peroxidic salts such as ammonium or sodium peroxydisulfate. The reaction can be initiated either by thermal or redox initiation. In thermal initiation the peroxydisulfate dissociates to give two SO^{4-} radicals.

$$\underset{\text{peroxydisulfate}}{{}^{-}O_3S{-}O{-}O{-}SO_3^{-}} \rightarrow \underset{\text{sulfate radical}}{2SO_4^{-\bullet}}$$

In redox initiation a reducing agent (usually Fe^{2+} or Ag^{+}) is used to provide one electron, causing the peroxydisulfate to dissociate into a sulfate radical and a sulfate ion.

$$Fe^{2+} + \underset{\text{peroxydisulfate}}{{}^{-}O_3S{-}O{-}O{-}SO_3^{-}} \rightarrow Fe^{3+} + \underset{\text{sulfate radical}}{SO_4^{-\bullet}} + SO_4^{2-}$$

Straight acrylics are polymer dispersions composed exclusively of acrylate and/or methacrylate monomers. Styrene acrylic copolymers contain styrene as well. For both types of copolymer there are a host of monomers which differ greatly as regards glass transition temperature and the polarity of the homopolymers preapared from them [39]. Table 2.1 shows some monomer's water solubility and Tg values. Monomer composition is determined specify according to application conditions.

Table 2.1 : Water solubilities and glass transition temperatures of the principal monomers for acrylic dispersions.

Monomer building blocks	Water solubility at 25°C in g/100 cm^3	Glass transition temperature (Tg) of the homopolymer °C
Methyl acrylate (MA)	5.2	22
Ethyl acrylate (EA)	1.6	-8
n-Butyl acrylate (nBA)	0.15	-43
Methyl metacrylate (MMA)	1.5	105
n-Butyl metacrylate (nBMA)	0.08	32
Styrene	0.02	107
Acrylonitrile	8.3	105
Vinyl acetate	2.4	42

The special features of the polyacrylates and polymethacrylates that justify their relatively high price are the generally very good weatherability and UV stability, high transparency, good water resistance and yellowing resistance, great ease of variation in toughness, hardness and flexibility [40].

Special polymerization technique can be used in emulsion polymerization that comes from morphology of polymerization. Different kind of morphology is used in emulsion polymerization technology such as core-shell, raspberry, half-moon shaped particles. Core-shell technology is one of the most widely used methods in polymerization. By combining a soft, film forming occurs at low temperature, and a hard monomer, which film formation occurs at high temperature in one and the same particle, and by tailoring the particle morphology, it is even possible to achieve better polymer specialty. Such this core-shell system have a low MFFT and high elasticity, along with good freedom from tackiness, excellent blocking resistance and good coating hardness. Especially for the special coating application systems such as wood coating, metal coating, joinery, core-shell morphology is preferred [41,42].

Acrylic resins are composed mainly esters of acrylic acids or methacrylic acid. They are generally used in paint and coating industries. Also they can be used in textile, adhesive, printing inks, paper coating and construction industries. Acrylic esters and methacrylic esters have quite different properties. Amount of these esters in polymer specify material properties, hardness, flexibility, chemical resistance, leveling during film formation [43].

Esters of acrylic acid or methacrylic acid are distinguished by the reactivity of their double bonds. After initiation these double bonds connect each other and polymerization occurs. Esters of acrylic acid and metacrylic acid which act as building blocks for polymers are called monomers. Further building blocks capable of forming polymers conjuction with acrylic and metacrylic esters are called comonomers [44,45].

Water-borne acrylic dispersions are commonly prepared via emulsion polymerization. Emulsion polymerization has more advantages in comparison to solution polymerization. First of all, much higher molecular weight polymers can be synthesis. High solid content (50% or higher) polymers can be produced with emulsion polymerization. Another advantage is that the resin has low viscosity, thus allowing fast air drying by evaporation of water [46,47].

2.1.4 Emulsion copolymerization

In many cases latex products are composed of more than one monomer. In copolymerization two or more monomers are incorporated into the polymer chains. The copolymer chains are produced by simultaneous polymerization of two or more monomers in emulsion. Emulsion copolymerization allows the production of materials with properties which cannot be obtained by latex products consisting of one monomer, that is, homopolymer latexes, or by blending homopolymers. The properties of the materials required are usually dictated by the market. Nowadays most of the materials properties are achieved by combination of more than two monomers in the copolymer product. Typical industrial emulsion polymerization formulations are mixtures of monomers giving hard polymers, and monomers leading to soft polymers. Styrene and methyl methacrylate are examples of monomers giving hard polymers, that is, polymers with a high glass transition temperature, T_g. Soft polymers, that is, polymers with a low T_g, are, for example, formed from n-butyl acrylate. The industrial emulsion polymerization formulations also contain small amounts of functional monomers, such as acrylic and methacrylic acid, to impart improved or special characteristics to the latex product. Note that the colloidal stability of the latex product can be seriously improved by acrylic and methacrylic acid. Furthermore, some applications may demand the addition of other specialty monomers which make the kinetics of the copolymerization even more complex [30].

Vast amounts of polymers generated by emulsion polymerization are copolymers as the properties of the individual polymers can be synergistically increased by the generation of copolymers. However, as the different monomers have different reactivities in a particular system therefore there it is always complex to predict the final composition of the copolymer chains and if it would be same as the initial monomer ratios. Apart from that, as the reactivities are different from each other, the more reactive monomer may polymerize first, thus forming core of the particles rich in this polymer followed by an outer cover of particles more rich in less reactive monomers. This leads to a gradient of concentration of different monomers on these particles. There can similarly be also differences when the water solubilities of the monomers are quite different from each other. Figure 2.4 is an example of comparison of the homopolymers with copolymers. The pure polystyrene particles shown in Figure

2.5 are compared with the copolymers of styrene with water soluble monomer N-isopropylacrylamide.

Figure 2.4 : SEM images of styren-co-isopropylacrylamide copolymer particles.

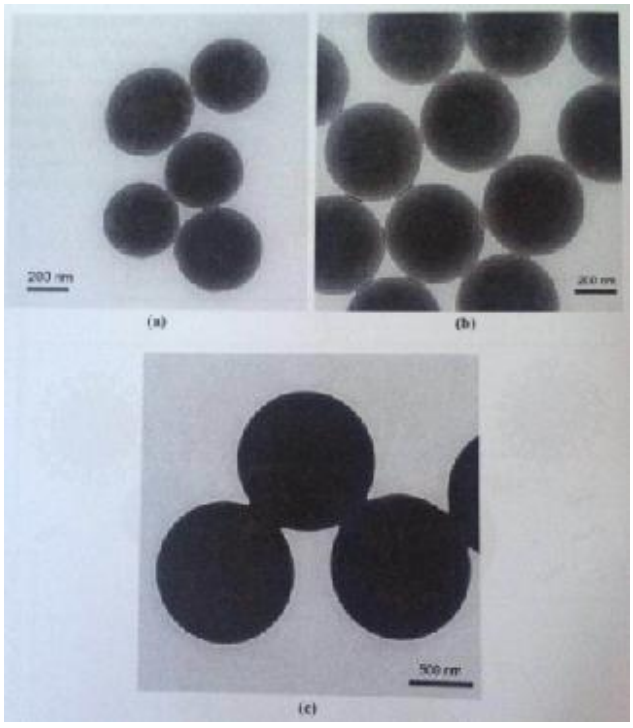


Figure 2.5 : Evolution of particle size as a function of conversion.

The generated surface morphology is totally different in these particles. One should note here that the particles were achieved without using the surfactant, i.e. particle generation was achieved by homogeneous nucleation mode. The more hydrophilic monomer starts polymerizing first followed by the polymerization of more hydrophobic monomer. The hydrophobic monomer polymerize inside these particles because of the hydrophobicity thus pushing the hydrophilic chains of poly(N-isoporopylacrylamide) on the surface of the particles.

Monomer portioning is the term most commonly used to describe the emulsion copolymerization of two or more monomers. Owing to the different reactivity ratios of the monomers and the different ratio of monomers in the polymer particles (i.e., loci of polymerization), which is generally very different from the initial monomer ratios, the compositional drift in the copolymer composition takes place [29].

2.1.5 Core-shell morphology

Special polymerization technique can be used in emulsion polymerization that comes from morphology of polymerization. Different kind of morphology is used in emulsion polymerization technology such as core-shell, raspberry, half-moon shaped particles. Core-shell technology is one of the most widely used methods in polymerization. By combining a soft, film forming occurs at low temperature, and a hard monomer, which film formation occurs at high temperature in one and the same particle, and by tailoring the particle morphology, it is even possible to achieve better polymer specialty. Such this core-shell system has a low MFFT and high elasticity, along with good freedom from tackiness, excellent blocking resistance and good coating hardness. Especially for the special coating application systems such as wood coating, metal coating, joinery, core-shell morphology is preferred [42,43].

The design of the core-shell particles are dictated by the desired properties and applications. The properties that core-shell latex particles exhibit depends on a number of parameters, such as the polymer or copolymer type, the molar mass, the amount of grafted material between the core and the shell, the particle size and particle size distribution, the relative proportion of the core to the shell material, the glass transition temperature T_g of the polymer in the core and in the shell. Three main types of core-shell composite particles can be distinguished, viz. composite particles with organic cores, with inorganic cores and those with an ‘empty’ core, the so-called hollow

particles. Hard core-soft shell particles are used for high performance coatings, with the soft shell forming the film and the hard core imparting mechanical resistance to the film. Soft core-hard shell particles are used as impact modifiers for brittle polymers such as poly(vinyl chloride) and polycarbonate [30].

2.2 Surfactants

Surface active substances or surfactants are amphiphilic compounds having a lyophilic, inparticular hydrophilic, part (polar group) and a lyophobic, in particular hydrophobic, part (often hydrocarbon chain). The amphiphilic structure of surfactants is responsible for their tendency to concentrate at interfaces and to aggregate in solutions into various supramolecular structures, such as micelles and bilayers[48].

Surfactants are mostly classified according to the hydrophilic group (Figure 2.6):

- Anionic surfactants, where the hydrophilic part is an anion
- Cationic surfactants, where the hydrophilic part is a cation
- Amphoteric surfactants, where the properties of the hydrophilic function depend on the pH,
- Non-ionic surfactants, where the hydrophilic part is a non-ionic component, for instance polyols, sugar derivatives or chains of ethylene oxide. [30]

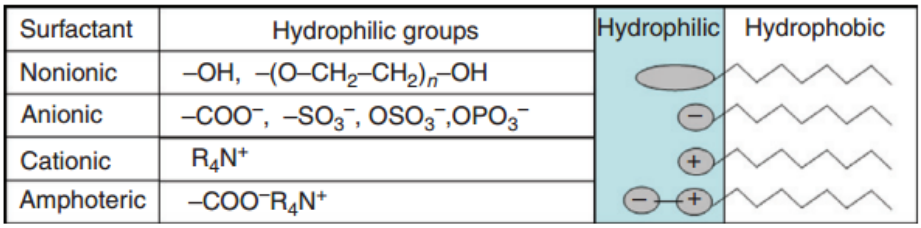


Figure 2.6 : Classification of surfactants.

2.2.1 Anionic surfactants

Anionic surfactants are amphiphilic substances that include an anionic group as an obligatory component attached directly or through intermediates to a long hydrocarbon chain [48].

The hydrophilic head groups of the anionic surfactants are negatively charged and comprise sulfate, sulfonate, sulfosuccinate, or phosphate groups which are attached to an extended hydrophobic backbone. The nature of the negatively charged hydrophilic group is important because it influences the extent of electrostatic stabilization, the

behavior of the emulsifier as a function of solution pH, and the variation of the polyVAc latex stability with time, electrolyte, and temperature conditions. The nature of the hydrophobic backbone affects the critical micelle concentration (CMC) value of the emulsifier, the interfacial tension between the water and the monomer which influences the emulsification of the monomer, the adsorption behavior of the emulsifier on the latex particle surface, and the extent of steric stabilization [49].

2.2.1.1 Sodium alcohol sulfate

Sodium lauryl (dodecyl) sulfate, [$C_{12}H_{25}OSO_3^-$ Na^+], is one of the most commonly used anionic emulsion polymerization surfactants having a sulfate ionic group. It has a CMC of 0.060–0.085 wt% in water, according to the manufacturer.

2.2.1.2 Alkyl aryl sodium sulfonate

Sodium dodecylbenzene sulfonate, [$C_{12}H_{25}C_6H_4SO_3^-$ Na^+], has a sulfonate ionic group. Its CMC varies between 0.10–0.12 wt % according to the manufacturer. Two sulfonate groups per emulsifier molecule were also synthesized. Alkylated disulfonated diphenyl oxide emulsifiers with C_6–C_{16} hydrophobic groups (both linear and branched) are manufactured with CMC's ranging from 0.05 to 1.90 wt% depending on the hydrophobic group.

Sulfonate emulsifiers have an advantage over sulfate emulsifiers in that they are less susceptible to hydrolysis under acidic conditions. The hydrolysis reaction separates the polar hydrophilic group from the hydrophobic group by cleavage of the C-O-S bond in the sulfates, and thus destroys its function as an efficient emulsifier. However, the equivalent bond in sulfonates is C-S, which is not so susceptible to acid hydrolysis.

2.2.1.3 Dialkyl ester of sodium sulfosuccinic acid

Sodium dioctyl sulfosuccinate, [$(C_8H_{17}COOCH_2)_2SO^{3-}$ Na^+], is a very commonly utilized emulsifier and has a CMC of 0.07 wt%, whereas its homologues, sodium dihexyl sulfosuccinate with its CMC = 1.0 wt% and sodium diamyl sulfosuccinate with its CMC = 1.2 wt%, are also used in emulsion polymerizations. Another derivative of sulfosuccinate is a polymerizable emulsifier, sodium dodecyl allyl sulfosuccinate, which was studied extensively by Urgiola et al. in the emulsion polymerization of VAc. They determined that a significant degree of chain transfer to the emulsifier occurs, which explains the decrease in the polymerization rate with

increasing emulsifier concentration. This behavior is opposite to the usual observation with conventional emulsifiers.

2.2.1.4 Fluorinated anionic emulsifiers

A series of fluorinated anionic emulsifiers was synthesized in which a fluorocarbon group replaced the hydrophobic tail in the emulsifier molecule containing a sulfonate hydrophilic group. Ammonium perfluoroalkyl sulfonate can be used in acrylic-based emulsions, which lower the surface tension of the aqueous phase much larger than equivalent hydrocarbon-based emulsifiers.

2.2.2 Phosphate ester anionic emulsifiers

When ethoxylated nonyl phenol groups are combined with phosphate anionic groups, phosphate ester anionic emulsifiers are obtained such as nonyl phenol ethoxy (6) phosphate ester with a CMC of 0.022 wt%. This emulsifier can be used in the emulsion polymerization of VAc and VAc-acrylic copolymers [49].

2.2.3 Cationic surfactants

A surfactant is classified as cationic if its molecule can dissociate in solution forming a surface active cation and normal anion. According to the chemical structure, cationic surfactants are subdivided into the following main classes: alkyl amines, ethoxylated amines, alkyl imidazolines, and quaternaries [48].

Salts of long chain amines, polyamine salts, polyoxyethylenated long-chain amines and their quarternized derivatives, and amine oxides are also used as cationic emulsifiers.

Cationics are used in specialty applications where it is desirable to impart a positive charge on emulsion particles. Cationic emulsifiers are only infrequently used in VAc emulsion polymerization because they are not compatible with anionic emulsifiers or negatively charged latex particles [49].

2.2.4 Non-ionic surfactants

Nonionic surfactants are amphiphilic compounds the lyophilic (in particular hydrophilic) part of which does not dissociate into ions and hence has no charge. However, there are nonionics, for example such as tertiary amine oxides, which are able to acquire a charge depending on the pH value. Even polyethers, such as

polyethylene oxides, are protonated under acidic conditions and exist in cationic form. Long-chain carboxylic acids are nonionic under neutral and acidic conditions whereas they are anionics under basic conditions. So, the more accurate definition is as follows: nonionics are surfactants that have no charge in the predominant working range of pH. The main part of nonionics can be classified into alcohols, polyethers, esters, or their combinations [48].

Nonionic emulsifiers, which carry essentially no charge, overcome the incompatibility exhibited by ionic emulsifiers when certain additives are used in compounding.

They usually produce latices of rather large particle size. Nonionic emulsifiers are generally characterized by a simple method called "cloud-point determination." The cloud-point is a measure of the inverse solubility of the nonionics with temperature, and is usually determined by heating 1 wt% solution of the emulsifier in water in a test tube until it clouds, and then measuring the temperature at which clearing occurs as the solution cools. In most cases, no difference is found between a cloud-point measured in rising or falling temperature. At the cloud-point, the sudden onset of turbidity of the nonionic solution takes place, and at somewhat higher temperatures the solution begins to separate into two phases. In one of them, the emulsifier concentration is enriched, whereas in the other it is depleted. The cloud-point method determination serves both as a control method and as a specification for nonionic emulsifiers.

2.2.4.1 Polyoxyethylenated alkylphenol nonionic emulsifiers

Ethylene oxide adducts of alkyl aryl phenols are examples of this type. Nonylphenol polyoxyethylene glycol, $[C_9H_{17}C_6H_4O–(CH_2CH_2–O)_nH]$, and octylphenol olyoxyethylene glycol, $[C_8H_{15}C_6H_4O–(CH_2CH_2–O)_nH]$, are the main members of this group. The number of ethylene oxide units, (n), may be varied from a few to about 100 (typically from 1 to 70 EO units), which characterize the distribution of polyEO chain lengths for each specific emulsifier and produce a wide range of surfactant properties. The lower EO unit numbers are oil-soluble, while the higher are watersoluble. As the length of the ethylene oxide side chain is increased, uses gradate from water-in-oil emulsions through wetting agents, oil-in water emulsions, and detergents to solubilizers. These emulsifiers are supplied having various activities ranging from 20 to 100%. The CMC value of 30–40 moles of EO for octylphenol is in the 0.03–0.04

wt% range, whereas the CMC value of 9–100 moles of EO for nonylphenol is in the 0.005–0.100 wt% range.188 The HLB value increases with the increase in EO units in the emulsifier. Typically, the HLB value of 4 moles ethoxylated nonylphenol emulsifier is 8.7, whereas it increases up to 18 for the 40 moles ethoxylated one. Thus, all the nonylphenol emulsifiers having more than 4 EO units are considered essentially hydrophilic. The higher adducts containing 20 to 100 moles of ethylene oxide are used in the emulsion polymerization of VAc and acrylates.

By judicious choice of these nonionics, or by use of blends of high, intermediate, and low ethylene oxide substituted ones, it is possible to alter latex properties such as particle size, viscosity, freeze-thaw stability, film clarity, water resistance, and rates of monomer conversion. However, most emulsifiers are water soluble and contribute to the water sensitivity of a film deposited from the emulsion. If, therefore, the end use of the emulsion is to prepare water-resistant films, the emulsifier concentration used should be kept at a minimum.

2.2.4.2 Polyoxyethylenated alcohol nonionic emulsifiers

Ethylene oxide adducts of straight chain primary alcohols such as n-decanol, n-dodecanol, n-tetradecanol, and n-octadecanol are examples of this type, [RO–$(CH_2CH_2O)_nH$]. These emulsifiers can be biodegradable and are favored due to environmental aspects. Ethylene oxide adducts of fatty alcohols are also used as surfactants in emulsion polymerization because of their tolerance for hard water and their imparting shear resistance to latex.

2.2.4.3 Ethylene oxide-propylene oxide block copolymer nonionic emulsifiers

Polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymers are examples of this type: [H–$(OCH_2CH_2)_a$–$(OCH_3CH–CH_2)_b$–$(OCH_2CH_2)_a$–OH]. The polyethylene oxide portion constitutes between 10 and 80% of the copolymer.

Emulsifiers having their HLB value greater than 24 are used in emulsion polymerizations. Their use in industry is due in part to their low foam level, and in part on their preventing the agglomeration of pigment particles on addition to aqueous systems when the latex is used as a paint binder. Using polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymer surfactant as the sole emulsifier in VAc emulsion polymerization, the molecular weight of the VAc polymer

increases and the latex particle size decreases as the concentration of the surfactant containing 80 wt% polyoxyethylene (HLB value = 27) is increased from 2.5 to 7.5%. Tetrafunctional block copolymers are also synthesized by the polycondensation of polypropylene oxide and polyethylene oxide on ethylene diamine: $[H(C_2H_4O)_y(C_3H_6O)_x]_2–N–CH_2–CH_2–N–[(C_3H_6O)_x(C_2H_4O)_yH]_2$. The addition of these emulsifiers decreases the water sensitivity and enhances freeze-thaw, shear, and electrolyte stability. They also result in low foam formation during emulsion polymerization.

2.2.4.4 Other nonionic emulsifiers

Polyoxyethylenated fatty acid esters, alkanolamine condensates, tertiary acetylenic glycols, alkylpolyglycosides, polyoxyethylenated mercaptans, polyoxyethylenated silicones, n-alkylpyrollidones, polyoxyethylenated alkylamides, and amines are considered nonionic emulsifiers [49].

2.2.5 Amphoteric and zwitterionic surfactants

An amphiphilic compound is named amphoteric surfactant if its functional group is capable of carrying both anionic and cationic charges. The term "amphoteric surfactants" or "amphoterics" is referred generally to compounds that show pH-dependent amphoteric properties. However, there are amphiphiles containing both strongly acidic and strongly basic groups, such as the sulphonic group and quaternary ammonium group, respectively. Those amphiphiles show both anionic and cationic properties independent of the pH and they were specified as zwitter-ionic surfactants [48].

Amphoteric (zwitterionic) emulsifiers show anionic properties at high pH and cationic properties at low pH. They are mainly alkylamino or alkylimino propionic acids. These surfactants are not commonly used in emulsion polymerization recipes [49].

2.2.6 Surfactants in emulsion polymerization

Surfactants are employed in emulsion polymerizations to facilitate emulsification and impart electrostatic and steric stabilization to the polymer particles.

Electrostatic stabilizers are usually anionic surfactants, i.e., salts of organic acids, which provide colloidal stability by electrostatic repulsion of charges on the particle

surfaces and their associated double layers. Cationic surfactants are not commonly used in emulsion polymerizations [34].

Emulsifying agents in emulsion polymerizations serve to reduce the interfacial tension between the monomer phase and the water phase so that, with agitation, the monomer is dispersed (or emulsified) in the water phase. In general, the amount of emulsifier used influences the average size of the final latex particle. As a rule, a large quantity of emulsifier will produce small polymer particles, and a small amount of emulsifier will produce large polymer particles. Thus, in order to decrease the particle size and increase latex viscosity, an increase in the quantity of emulsifier is required. Anionic and nonionic emulsifiers in concentrations of 0.05 to 2.00% by weight are generally added for the emulsion polymerization of vinyl acetate. These concentrations correspond to 0.1 to 4.0% by weight to monomer (lower concentrations for the anionic emulsifiers and higher for the nonionics).

Emulsifiers (or surfactants, soaps, dispersing agents, detergents) perform the most important function of all in producing fine particle dispersions. They act to stabilize the monomer droplets in an emulsion form, serve to solubilize monomer within micelles, stabilize the formed monomer-swollen polymer particle during propagation and after the polymerization process, act to solubilize the polymer in aqueous phase to a lesser extent, sometimes serve as the site for the nucleation of particles, and sometimes act as chain transfer agents and retarders.

Emulsifiers owe their unique properties to the presence in one molecule of two well-separated groups: a nonpolar (hydrophobic or oil-soluble) group and a polar (hydrophilic or water-soluble) group. At a concentration above a minimum (critical micelle concentration), characteristic of every surfactant, aggregation of the discrete molecules occurs to form micelles. These micelles are composed of a certain number of surfactant molecules in which the oil-soluble ends (tails) are directed inward toward the center, with the water-soluble ends (heads) on the periphery nearest the water atmosphere. Monomer diffuses from droplets in the mixture through the aqueous phase and into the micelles. Micelles continue to swell as polymer is formed and more of the monomer diffuses in. Finally, the micelle structure is destroyed and the surfactant molecules remain on the polymer particles as unimolecular absorbed layers. Monomer will then continue to diffuse into these particles and polymerize until conversion is complete.

The mixtures of different kind of surfactants (i.e., mixtures of nonionic and anionic emulsifiers) are often used together in a synergistic manner to control the particle size and to impart enhanced colloidal stability to the latex with regard to electrolyte differences, extremes in temperatures, and mechanical shearing effects. There is an enormous variety of commercial surfactants that are employed in the formulation of emulsion polymerizations. McCutcheon's publishes an extensive compilation listing a wide variety of surfactants and their manufacturers' information. Commercial emulsifiers often comprise a distribution of many different homologue molecules (i.e., in ethoxylated nonionic emulsifiers with ethylene oxide (EO) units present, the number of EO units per emulsifier molecule may vary, as can the alkyl lengths). This often results at the emulsifier manufacturing step where a distribution of EO and alkyl chain lengths in the emulsifier feed stock is used. The presence of the distribution of these homologues, and the by-products in the commercial emulsifier resulting from the manufacturing process (e.g., salts, alcohols, fats, etc.), may influence the kinetics of emulsion polymerization and, thus, the properties of the final latex.

There is a need for a method to predict the efficiency of emulsification for a given surfactant. HLB [hydrophile-lipophile (hydrophobe)] balance of the polar hydrophilic head and nonpolar lipophilic tail components in an emulsifier molecule system developed for this purpose in the late 1940s expresses the size and strength of the water-soluble and oil-soluble portions of the molecule.

HLB method is represented by an arbitrary scale in which the least hydrophilic materials have low HLB values, and increasing HLB corresponds to increasingly hydrophilic character. In general, emulsifiers with low HLB values (numbers less than 6 or 7) are defined as hydrophobic and are used as water-in-oil emulsifiers, while those with high HLB values (numbers greater than 8) are hydrophilic and good for oil-inwater emulsions such as polyVAc latices. The use of this system for selecting emulsifiers to be used in emulsion polymerization formulations has met mixed success. In general, emulsifier selection is still quite empirical and the experience of the formulator or trial-and-error approaches dominate in this field. In the 1990s it was found that surfactant adsorption energies were strongly correlated with the latex particle size obtained from emulsion polymerization, which may be a promising method for the future [49].

There is a very special connection between emulsion polymerization and emulsifiers originating from the fact that emulsifiers have a direct influence on the course of the polymerization, the properties of the dispersions, and the properties during the final applications. Consequently, one of the most common problems in the industrial world of emulsion polymerizations is that of matching a polymer dispersion formulation by making a proper choice of surfactant or surfactant combination to obtain a required end effect. This has been known in industry since the 1930s [50], and dealing with surfactants plays a major role in the industrial preparation of polymer dispersions. The application of surfactants in polymer dispersions has a bivalent character as the demands upon the surfactants during the polymerization and during the application are contradictory.

All advantages of the emulsion polymerization techniques are directly connected with the dispersed state and hence with the colloidal stability and the stabilizing system. Some important advantages are [51]:

- The existence of a thermodynamically stable large interfacial area in an aqueous environment allows easy removal of the polymerization heat.
- The viscosity of the dispersion medium is low and independent of the degree of polymerization of the polymer formed.
- The monomer consumption takes place outside the monomer phase, thus allowing feed procedures and hot cooling as result of which control of the polymerization is possible.
- Control of the monomer concentration at the main reaction locus is possible in such a way that the reactor can operate constantly at the maximum rate of polymerization.
- It is possible to carry out with comparably little technical effort batch, semibatch, and continuous polymerizations in which the feed of any additional components is possible.
- The particle size and the size distribution can be tailored in a desired range between 50 nm and 10 μm.
- The use of emulsifiers, water-soluble polymers, or other auxiliary materials offers further possibilities to modify the product properties.

In conclusion, any new surfactant for an emulsion polymerization is faced with the problem that it is only an auxiliary agent that has to meet strict cost requirements and

has to improve existing solutions in two contradictory fields (polymerization and application), but this is also a challenge for further research [52].

Other types of surfactants are the polymeric (steric) stabilizers such as partially hydrolyzed polyvinyl acetate. Also oligomeric species formed in situ, when $SO^{4-\bullet}$ radicals react with some monomer units in the aqueous phase, will have surface active properties, and can even form a colloidally stable latex. Electrosteric stabilizers combine steric and electrostatic functionalities: for example, inclusion of acrylic acid in a recipe results in chains with blocks comprised largely of poly(acrylic acid) which, in the aqueous phase, then pick up enough hydrophobic monomer to enter the particle and continue polymerization in the particle interior. The hydrophilic component remains in the aqueous phase and provides colloidal stability both sterically and, under the appropriate conditions of pH, electrostatically. This mode of stabilization is very common in surface coatings, because it gives excellent freeze–thaw stability. Common anionic surfactants include sodium dodecyl sulfate (SDS) and the Aerosol series (sodium dialkyl sulfosuccinates), such as Aerosol OT (AOT, sodium di(2ethylhexyl)sulfosuccinate) and Aerosol MA (AMA, sodium dihexyl sulfosuccinate). These particular surfactants tend to result in monodisperse latexes [30].

2.2.7 Green surfactants in emulsion polymerization

Surfactants monitor the emulsion polymerization process and stabilize the final latex. However, they are not part of the polymer. Because in many applications of polymer dispersions they are in direct contact with the environment, their ecotoxicological profile, more particularly the biodegradability of emulsifiers for emulsion polymerization, is of great importance. Biodegradability of chemical substances depends on their chemical structure. Branched hydrocarbon chains show poor biodegradability, particularly under anaerobic conditions. The nature of renewable raw materials especially fulfills the requirement for biodegradability under aerobic and anaerobic conditions. The linear hydrocarbon chains facilitate biodegradability, for example, of fatty alcohol sulfates and fatty alcohol polyglycol ethers, without the formation of ecotoxic metabolites as is the case with alkylphenol polyglycolethers which have been the workhorse as nonionic emulsifiers for years. Thus, the new

‘green’ emulsifiers based on renewable resources are increasingly replacing the alkylphenol ethoxylates (APEO) technology [53].

Driven by the personal care and cleaning applications, new and better performed surfactants were also introduced for technical purposes, even if alkylphenol ethoxylates are widely used as secondary surfactants in the emulsion polymerization process, as they are reasonably economic and have good stabilizing properties for a variety of monomers. Because of the concerns about the discussed alkylphenol residues, which are formed when these surfactants are released into the environment, many recipes have been reformulated to fatty alcohol ethoxylates [54,55]. Although great success has been achieved, there is still a long way to go. Besides the ecotoxicological arguments, the performances during the polymerization process and in the following coating and/or adhesive application tests are the main reasons why success is still limited at the moment. The surfactant properties of products based on methyl esters for example have been described and their performance attributes in emulsion polymerization and in paint applications [56]. Different nonionic products based on sugar surfactants were used in acrylate formulations with some good results but showing less water resistance [57].

For anionic systems, products based on sulfosuccinates are also playing an important role as alternatives to anionic APEOs. A summary for the use of these chemical products in the emulsion polymerization process is given [58].

Other surfactants based on tridecyl alcohol ethoxylates or synthetic secondary alcohol ethoxylates are also announced to be used for emulsion polymerization processes in the annual listing of commercial surfactants [59].

2.3 Wood Coatings

Wood has many diverse uses, some of which require coating for protective or decorative purposes. End-use sectors are usefully assessed in categories that can be related to the types of coating required. For example, meaningful distinction can be made between interior and exterior applications, the latter being much more demanding in terms of resistance to moisture and solar radiation. Another important distinction is between ‘decorative’ and ‘industrial’ applications. The term ‘decorative’ is widely used to denote coatings designed for buildings, known in some countries as

'Architectural Coatings'. Such coatings account for more than half of all coating production. The decorative sector may be split into a Professional (Trade) and Retail (DIY) sector. The distinction is not always sharp and can vary from 60:40 to 30:70 according to country [60]. Decorative coatings are applied by hand and are air-drying. This is in contrast to the industrial sector, which uses a wider range of application techniques and products that may require stoving or radiation curing. In the building application, there is overlap between decorative and industrial end-use categories, in that products originally coated in a factory, for example, windows may require subsequent maintenance in situ.

Moreover, wood coatings straddle the industrial and decorative sectors of joinery, but may be dealt with as 'industrial finishes' when describing furniture coatings. Flooring presents another difficulty since it may be coated industrially or in situ. There is also a growing sector of products used outdoors but more as part of garden rather than house decor. These will include coatings for decking, and brighter non-traditional colours used on fences for decorative rather than protective purposes. It should also be noted that volume can be expressed in different units such as weight, volume or monetary value in absolute or relative (percentage) terms. This may obscure growth trends as new sectors are defined, or as higher solids replace lower or indeed as margins are squeezed [61].

2.3.1 Composition of wood

Wood is composed of mainly three major polymers (cellulose, hemicelluloses, and lignin) and some extraneous substances called extractives. Table 2.2 lists the variation of these components in softwood and hardwood for five wood species each [62]. The combined polysaccharide components (cellulose plus hemicelluloses) often termed as holocellulose account for about 75% of the wood materials.

Table 2.2 : Chemical composition of wood.

Component	Softwood (%)	Hardwood (%)
Cellulose	42	42
Hemicellulose		
Xylan	10	20-35
Glucomannan	20	3-4
Lignin	25-35	18-25
Extractives	2-5	2-4

Major uses of these polysaccharide components have been in the form of fibers for making paper, paperboard, and other fiber products by the paper industry. Recently, the potential utilization of woody polysaccharides as feedstock for conversion to biofuels and chemicals has been examined quite extensively [63, 64].

Higher plants commonly are referred to as lignocellulosic materials because of the typical joint occurrence in them of lignin and cellulose. Lignin being a phenolic polymer is often considered as the gluing or encrusting substance of wood cells and adds mechanical strength or stiffness to the tree and wood. Lignin usually plays a negative role in the chemical utilization of woody materials and must be modified, partially degraded, or completely removed depending on the end uses of the final products. These lignin modification or delignification reactions constitute the commercial pulping and bleaching operations in producing papermaking fibers [65].

2.3.2 Wood coating systems

The wood-coating sector uses many different types of resin and polymer under such headings as ‘nitrocellulose’, ‘alkyd’, ‘acrylic’, ‘polyester’, ‘polyurethane’, etc. However, chemical terminology does not describe the technological factors that are important and cover the means by which a particular chemistry is delivered, and in some cases converted, from a liquid to a solid film.

The choice of technology for the wood-coatings market as illustrated in Figure 2.7 is clearly governed my many economic, commercial and operational factors.

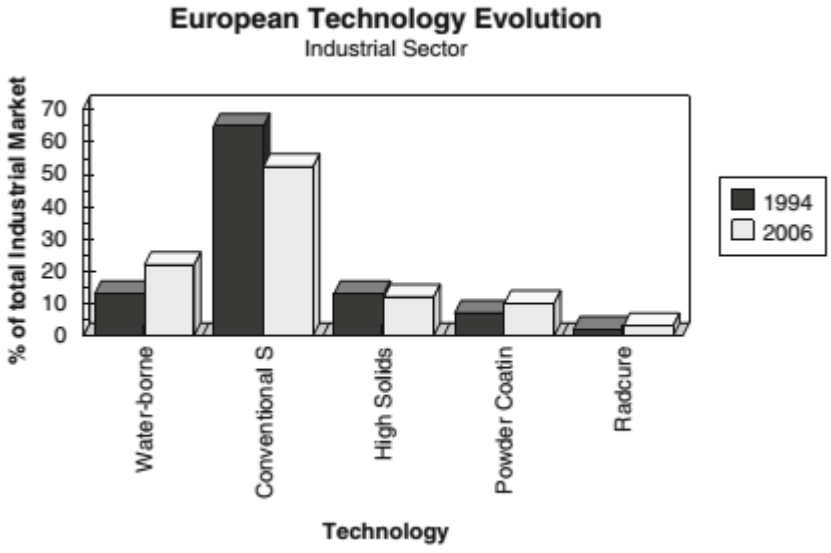


Figure 2.7 : Market share of wood coating systems.

In addition, there is the overarching requirement to meet current and proposed legislation. The list below shows the many legislative areas that have to be taken into account .

Legislative activity falls into three major categories:

(1) Global issues – for example, the impact of solvent on the environment including the ozone layer

(2) Local issues – for example, transport and waste regulations

(3) Personal issues – for example, the health of individuals exposed to coatings (occupational exposure)

The impact of the solvent emissions directive has created something of a crisis for industrial wood coating and in particular furniture. Traditionally, the furniture has used large amounts of solvent in quick-drying lacquer finishes such as nitrocellulose. Some solid contents are very low and range from 20% for nitrocellulose, 32% for acid cured technology, up to 40–70% for polyurethanes and polyesters. The remainder is solvent, which will also be used for cleaning purposes. UV and water-borne technologies could in principle contain no solvent, but many water-borne technologies contain up to 10%, and UV up to 25% [61].

2.3.3 Water-based wood coating systems

There are clearly environmental and other safety advantages in replacing solvent with water and this has been a major trend in the past decade. Unfortunately, water brings operational disadvantages and in the case of wood this includes increased grain-raising, and problems arising from the high latent heat of water particularly under industrial conditions. It is broadly true to say that the transition from solvent to water-borne requires retaining the advantages of the resins traditionally carried as solutions in solvent, whilst overcoming a number of operational disadvantages.

Generally speaking, most of the chemistries that have been described above can be translated to water. Rheology of the liquid material will often be different but the dried film will be generically similar. However in some cases, the different physical form of water-borne binders leads to a more open film morphology and differences such as water permeability can arise. The different approached to producing water-borne binders can be summarised as:

- Polymer synthesised in bulk, or solvent, and then transferred water:
  - By solubilisation and neutralisation
  - By emulsification

The former will give a solution or quasi-solution, while the later yields a true liquid in liquid emulsion:

- Polymer synthesised in the presence of water:
  - By emulsion polymerisation
  - Suspension polymerisation
  - Solution polymerisation

The process of emulsion polymerisation is the most important of these and despite the name yields a dispersion of polymeric particles. Rheological properties will thus be very different from a solution polymer. One important category of water-borne urethane resins, namely the polyurethane dispersions, is made by a combination of routes and involves both step and chain growth polymerisation. In all cases, high molecular weight resins (usually as dispersions) can be used without further cross-linking. However for low molecular weight resins and to enhance properties in general, some further cross-linking will be necessary. Thus, it may also be necessary to render the cross-linking agent water soluble or dispersible [66].

3. EXPERIMENTAL PART

Styrene acrylic polymers are synthesized by emulsion polymerization by using different anionic surfactants. Polymers are used as binders in water-based clear wood topcoat formulation for interior furniture applications. All formulations are evaluated in terms of physical, chemical and mechanical performances. The best performed formulation is selected and VTET, a Sulphur containing silane is incorporated in different ratios to the formulation via post-addition. VTET added formulations are also evaluated in terms of gloss, adhesion performance, hardness and scratch resistance.

3.1 Materials

Acrylic acid is a clear, colorless liquid with a characteristic acrid odor. It is miscible with water, alcohols and ethers. Acrylic acid as shown on Figure 3.1 will undergo the typical reactions of a carboxylic acid, as well as reactions of the double bond similar to those of the acrylate esters. It lends itself to polymer preparation as well as use as a chemical intermediate.

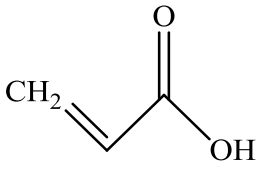


Figure 3.1 : Acrylic acid.

Acrylic acid provide electrosteric stabilization during the polymerization process. It is supplied by Arkema.

Styrene (CH_2=CH–C_6H_5), Methyl Methacrylate (CH_2=CH–$COOC_4H_9$) and Butyl Acrylate (CH_2=C(CH_3)–$COOC_2H_5$) are used as main monomers.

Styrene is a colorless to yellowish oily liquid with a distinctive aromatic odor. It is sparingly soluble in water.

Methyl Methacrylate is a very hard monomer, has good chemical resistance and weathering stability. Chemical composition of monomers are shown in Figure 3.2 in order.

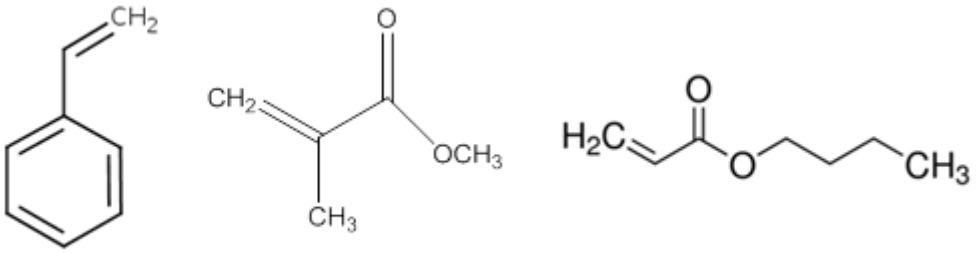


Figure 3.2 : Styrene, Methyl Methacrylate, Butyl Acrylate.

Water solubility, heat of polymerization and T_g of homopolymers of these monomers are given in Table 3.1.

Table 3.1 : Basic properties of monomers used in polymerization.

Monomer	T_g of homopolymer (°C)	Water solubility at 60°C (mol.%)	Heat of polymerization (kJ mol^{-1})
Styrene	100	0.041	70
Methyl Methacrylate	105	0.419	56
Butyl Acrylate	–54	0.0476	77

Sodium peroxide disulphate and *t*-butylhydroxyperoxide are used as initiators. Chemical structure is shown in Figure 3.3.

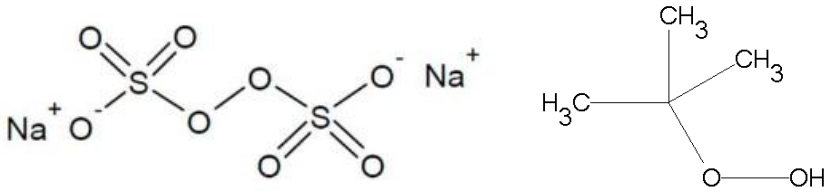


Figure 3.3 : Chemical structure of initiators - Sodium peroxide disulphate (left) *t*-butylhydroxyperoxide (right).

1,3-Butanediol Dimethacrylate (1,3-BDDMA) is used as cross-linker. Chemical structure of the cross-linker is shown in Figure 3.4.

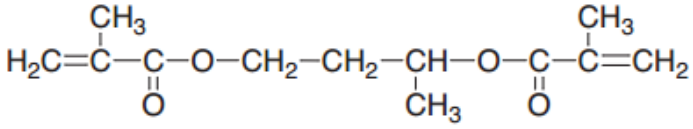


Figure 3.4 : Chemical structure of 1,3-Butanediol Dimethacrylate (1,3-BDDMA)

Sodium sulfoxylate is used as the oxidizer. Chemical structure is shown in Figure 3.5.

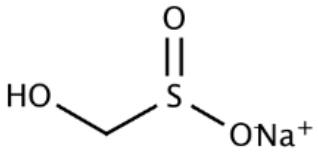


Figure 3.5 : Chemical structure of Sodium sulfoxylate

Coalescents, defoamers, wetting agents, thickener and neutralizing agents are used in clear wood topcoat formulation prepared with copolymers synthesized.

Butyl glycol and Dipropylene Glycol n-Butyl Ether (DPnB) are used as coalescents. Butyl Glycol has low volatility and acts as a coalescent and extend drying time. Its boiling point is 170°C. It is supplied by Basf. DPnB is a slow-evaporating, hydrophobic glycol ether with excellent surface tension-lowering ability and coalescing properties. Its boiling point is 230°C. DPnB is supplied by Dow Chemical.

BYK 348 and BYK 307 are used as wetting agents. BYK 348 is a silicone surfactant for aqueous systems. BYK 307 is a polyether modified polydimethylsiloxane. Both are supplied by BYK Chemie.

BYK 093 and Agitan 760 are used as defoamers. It is a VOC-free silicone-containing defoamer for aqueous wood coating and supplied by BYK Chemie.

Agitan 760 is a blend of modified organo polysiloxanes with nonionic alkoxylated compounds and highly effective siloxane defoamer for aqueous emulsion systems. It is supplied by Münzing Chemie.

AMP 90 is used as neutralizing agent. Its chemical structure is 2-Amino-2-methyl-1-propanol and supplied by Dow Chemical.

Rheolate 288 is used as thickener. It is a highly efficient polyether polyurethane associative thickener and supplied by Elementis.

VTET is a special, sulphur containing silane and used as a post-additive to analyse its effect on performance of clear wood topcoat. It is suppled by Polmag Research Laboratory of Istanbul Technical University. The structure of VTET is analysed by ^{1}H-NMR. Figure 3.6 shows the ^{1}H-NMR spectrum of VTET. According to the ^{1}H-NMR spectrum of VTET, chemical structure is proven as shown in Figure 3.7.

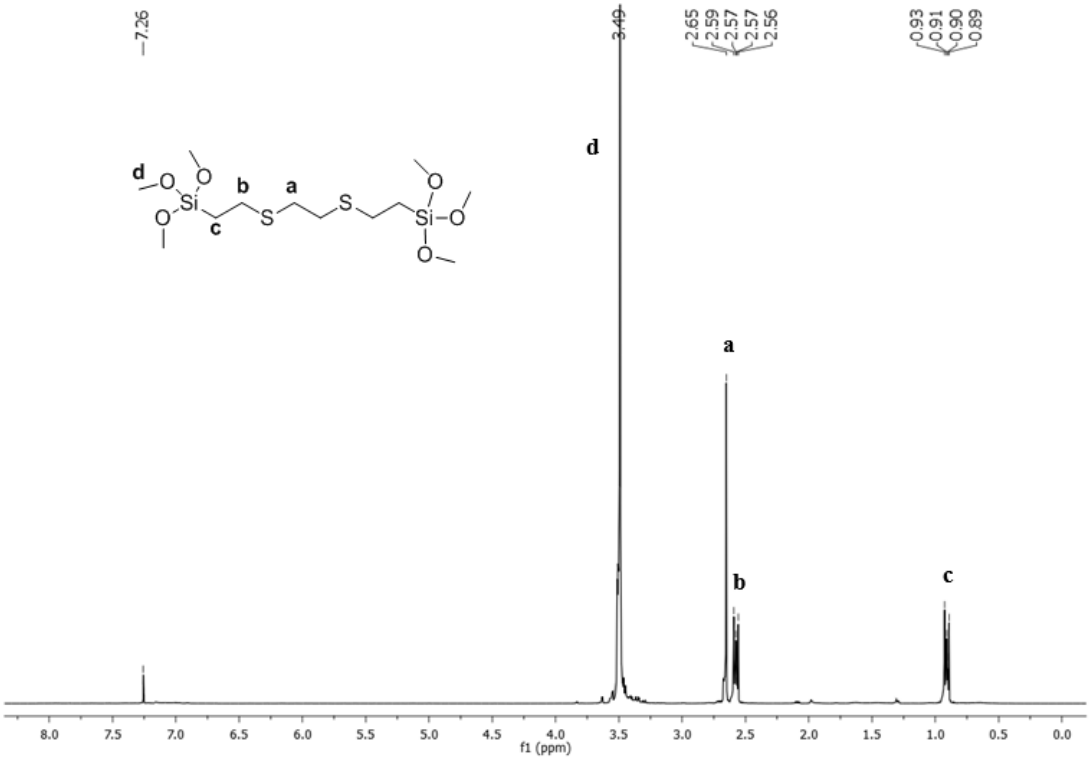


Figure 3.6 : 1H-NMR spectrum of VTET.

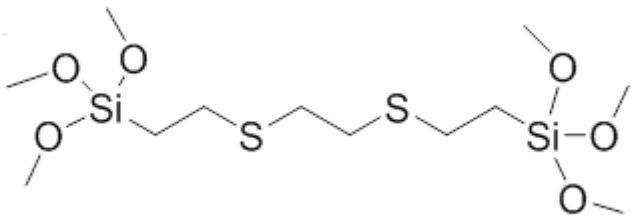


Figure 3.7 : Chemical structure of VTET.

3.2 Copolymer Synthesis

Copolymers are synthesized with the formulation shown in Table 3.2. Styrene (Sty), Methyl Methacrylate (MMA), Butyl Acrylate (BA) and Acrylic Acid are monomers, 1,3-ButanediolDimethacrylate (1,3-BDDMA) is the cross-linker, sodium peroxide

disulphate and tertiary butyl hydroperoxide (*t*-BHP) are used as initiators, sodium sulfoxylate is the oxidizer.

Table 3.2 : Copolymer formulation.

Ingredient	Part of weight (g)
Water	568
Styrene	159
Butyl Acrylate	140
Methyl Methacrylate	114
Acrylic Acid	4
1,3-BDDMA	2
Anionic surfactant, 100 % active substance	9
Sodium peroxide disulphate	2
t-BHP	0.5
Sodium sulfoxylate	0.5
Biocide	1

The morphology of the copolymers is core-shell. Because of the core-shell structure of the copolymers, two emulsions of monomers are prepared as E1 (Emulsion 1) and E2 (Emulsion 2). Table 3.3 shows the composition of E1 and E2.

Table 3.3 : Composition of Emulsion 1 and Emulsion 2

Emulsion 1	Emulsion 2
Water	Water
1,3-BDDMA	1,3-BDDMA
Anionic surfactant	Anionic surfactant
Main monomers (Sty, MMA, BA)	Main monomers, (Sty, MMA, BA)
Acrylic acid	Acrylic acid

Both emulsions contains Sty, MMA and BA as main monomers but ratios are different. E1 is rich in BA which makes the core of the copolymer softer, and E2 is rich in Sty which makes the shell of the copolymer harder.

Anionic surfactant is mixed with water and heated up to 85°C. 5% of E1 and intiators are incorporated to the mixture and the reaction initiates. Rest of E1 is fed for 1,5 hours with a constant temperature 80°C. Afterwards E2 is fed for 1,5 hours at 80°C. Thus, monomers are fed by 3 hours in total. The temperature is constant during monomer feeding. After monomer feeding, the system is cooled down to 70°C and oxidizer is incorporated to decrease free monomer content. In the end, pH is adjusted 8.0 with ammonia neutralizing agent.

3.3 Water-based clear wood topcoat formulation

Water-based clear wood topcoat formulation shown in Table 3.4 is selected as all the ingredients are compatible with seven copolymers synthesized. Topcoats are prepared for each copolymer with the same formulation to analyze the effect of different surfactants used in emulsion polymerization on performance of clear wood topcoat.

Table 3.4 : Water-based clear wood topcoat formulation.

Ingredients	Amount (%)
Copolymer	62,8
Butyl Glycol	3,5
DPnB	1,5
BYK 093	1
BYK 348	0,5
BYK 307	0,3
Agitan 760	0,5
Water	26,39
AMP 90	0,01
Rheolate 288 (50%)	3,5

Dispermat dissolver is used to prepare topcoats. All topcoats are prepared as 1 kg. First copolymer is weighed in a 2 lt stainless steel container and the container put under the dissolver. During the preparation, dissolver worked at 750 rpm. Afterwards other ingredients added slowly while dissolver is running. After pH adjustment with AMP 90, Rheolate 288 solution is incorperated slowly by checking the viscosity. It is added till the viscosity reaches 70 sn (Ford Cup 4).

4. RESULTS AND DISCUSSON

4.1 Analysis of Copolymers

Seven styrene-acrylic copolymers in core-shell morphology are synthesized with different anionic surfactants. Table 4.1 shows the surfactants used in copolymers.

Table 4.1 : Types of anionic surfactants used in emulsion polymerization.

Polymer #	Type of anionic surfactant
Copolymer 1	Sodium lauryl ether sulphate 2 EO
Copolymer 2	Alkyl polyethylene glycol ether sulphate
Copolymer 3	Sodium lauryl ether sulphate 4 EO
Copolymer 4	Polyoxyethylene tridecyl phosphate ester
Copolymer 5	sodium dodecylbenzene sulfonate
Copolymer 6	Disodium ethoxylated alcohol [C_{10}-C_{12}] half ester of sulfosuccinic acid
Copolymer 7	Sodium lauryl sulphate

Particle size of copolymers are analyzed by Malvern Mastersizer particle size analyzer.

Average particle size of the copolymers are shown in Table 4.2 particle size distribution graphs are given in Appendix A.

Table 4.2 : Average particle size of copolymers (d.nm).

Copolymer #	Average particle size (d.nm)
Copolymer 1	76,56
Copolymer 2	104,9
Copolymer 3	73,38
Copolymer 4	105,7
Copolymer 5	85,89
Copolymer 6	100,5
Copolymer 7	75,64

4.2 Performance Analysis of Clear Wood Topcoat

Water-based clear topcoat formulations are prepared and applied on beech veneer panels by spray application. First coat is applied as 200 µ and after 1 day, second coat is applied as 200 µ. Applied beech veneer panels are dried 7 days in climatic room

where temperature (25°C) and relative humidity (60 %) are stable. Some test are done on 1 day cured panels and some are done on 7 days cured panels.

Topcoats are numbered according to the polymers used in the formulation. As an example, in topcoat 1, polymer 1 is used as the binder.

4.2.1 Gloss

Gloss at 20°, 60° and 85° are measured with Novo-Gloss Trio Statistical Glossmeter on 7 days cured panels. Results are shown in Table 4.3.

Table 4.3 : Gloss results of applied topcoats on beech veneer panels.

Topcoat #	Gloss 20° / 60° / 85°
Topcoat 1	43,3 / 79,2 / 82,3
Topcoat 2	23,6 / 58,3 / 63,6
Topcoat 3	31 / 66,6 / 72
Topcoat 4	29,6 / 72,1 / 76,3
Topcoat 5	57,1 / 82,2 / 90,3
Topcoat 6	40,1 / 72,4 / 78,4
Topcoat 7	37 / 73,6 / 75,3

4.2.2 Hardness

Hardness is tested on both 1 day cured and 7 days cured panels. Persoz pendulum hardness results are shown in Table 4.4.

Table 4.4 : Persoz Pendulum hardness results.

Topcoat #	Hardness after 1 day (persoz)	Hardness after 7 days (persoz)
Topcoat 1	179	210
Topcoat 2	180	190
Topcoat 3	178	200
Topcoat 4	181	212
Topcoat 5	203	232
Topcoat 6	191	215
Topcoat 7	123	175

4.2.3 Coin resistance

It is similar to scratch resistance. The test is not done by an instrument. It is testing the hardness manually by a coin, scratching the topcoat film on wood strongly. The test is done to be able to compare the coin resistance of topcoats. Performance is ranked between 0 and 5. 5 is the best which shows high coin resistance. The results are shown in Table 4.5.

Table 4.5 : Coin resistance results.

Topcoat #	Coin resistance 0 – 5 (5 is the best)
Topcoat 1	2
Topcoat 2	3
Topcoat 3	5
Topcoat 4	4
Topcoat 5	3
Topcoat 6	5
Topcoat 7	5

4.2.4 Blocking resistance

Block resistance is the ability of a coating to resist sticking to another surface and to resist any change in appearance when it is pressed against that surface for a prolonged period of time.

Coated wood panels stacked face to face and pressure applied. After the pressure is released, coated surfaces are examined for any signs of sticking, damage or pressure mottling.

Blocking resistance of the topcoats first tested on lanetta after 1 day curing, both at room temperature and 40 °C. Results are shown in Table 4.6.

Table 4.6 : Blocking test results on lanetta after 1 day curing.

Topcoat #	Blocking at 23 °C	Blocking at 40 °C
Topcoat 1	10 / 10	10 / 10
Topcoat 2	10 / 10	10 / 10
Topcoat 3	10 / 10	10 / 10
Topcoat 4	10 / 10	10 / 10
Topcoat 5	10 / 10	10 / 10
Topcoat 6	10 / 10	10 / 10
Topcoat 7	10 / 10	10 / 10

However most of the coatings show good performance in standard blocking test, wood coatings are forced for further testing to be able to simulate the process in furniture industry.

Early blocking test is the hardest test method for water-based wood coatings. 3 panels are prepared for early blocking test. 200 µ wet film is applied by an applicator on a 10 cm × 10 cm sized mdf panel. After 5 min. flash at room temperature, panels are dried at 50°C drying oven for 20 min. Then the film is sanded and 150 µ wet film is applied again. After 5 min. flash of at room temperature, panels are dried at 50°C drying oven

for 20 min. Then coated face of two panels stacked together and third one is placed on the top where its coated side will face back side (mdf side) of the other. 2,5 kg weight is put on three panels and the pressure is applied for 16 hours. After 16 hours, 2,5 kg pressure is released and coated surfaces are examined for any signs of sticking, damage or pressure mottling.

Results are ranked from 0 to 10. If the panels can be separated very easily, without a force, and there is no noise, it is ranked 10. If all of the film is damaged, sticked together, it is ranked 0. Both topcoat to topcoat and topcoat to wood performances are evaluated. Results are shown in Table 4.7.

Table 4.7 : Early blocking test results.

Topcoat #	Early blocking resistance Topcoat to topcoat	Early blocking resistance Topcoat to wood
Topcoat 1	7	9
Topcoat 2	7	9
Topcoat 3	9	10
Topcoat 4	6	8
Topcoat 5	7	9
Topcoat 6	7	10
Topcoat 7	6	10

4.2.5 Chemical resistance

Chemical resistance is tested on spray applied beech veneer wood panel. Various chemicals are applied on 7 days dried film and performance is ranked between 1 and 5, ranking details are shown in Table 4.8.

Table 4.8 : Explanation and details of chemical resistance ranking system.

Rank	Explanation	Detail
1	Strong Change	Distinctive change in structure and/or change in gloss, color and discoloration, and/or paper adheres to surface and/or coating has peeled off
2	Significant Change	Change visible in all viewing directions, color change, gloss, discoloration, and/or also minor structure defects
3	Moderate Change	No change in surface structure: change only visible from several viewing directions, only color change, gloss, discoloration
4	Minor Change	No change in surface structure: change only visible from one viewing direction, only color change, gloss, discoloration
5	No change	No change

Chemical resistance test results are shown in Table 4.9. The sum is calculated at the end for each panel to be able to compare general chemical performance.

Table 4.9 : Chemical test results.

Chemicals – time	Topcoat #						
	# 1	# 2	# 3	# 4	# 5	# 6	# 7
Coffee 10 min*	5	5	5	5	5	5	5
Red Wine 10 min	5	5	5	5	5	5	5
Black Tee 10 min	5	5	5	5	5	5	5
Water 10 min	5	5	5	5	5	5	5
Acetic Acid 60 min	5	5	5	5	5	5	5
Cleaner 60 min	5	5	5	5	5	5	5
Ethanol 60 min	5	5	5	5	5	5	5
Acetone 10 sec	5	5	5	5	5	5	5
Ammonia 2 min	3	3	3	3	3	3	3
Red Wine 6 hrs	5	5	5	5	5	5	5
Mustard 6 hrs	5	5	5	5	5	5	5
Olive oil 16 hrs	5	5	5	5	5	5	5
Lipstick, 60 min	5	3	5	3	5	5	4
Coffee 16 hrs**	5	3	4	3	5	5	4
Cleaner 16 hrs**	5	5	4	5	3	5	5
Ethanol 16 hrs	4	5	5	5	5	4	4
Water 16 hrs	5	3	5	5	3	5	3
Hand cream, 16 hrs	5	5	5	5	5	5	5
TOTAL	87	82	86	84	84	87	88

4.3 The Effect of VTET in Water-based Clear Wood Topcoat

According to the performance tests done for the topcoats on wood, topcoat 3 performed best and selected to test the effect of VTET, sulphur containing silane, in water-based clear wood topcoat formulation.

VTET is incorporated in three different ratio as 0,1 %, 0,5 % and 1 % to the topcoat formulation prepared with copolymer 3.

4.3.1 Effect on colour of topcoat

It is observed that with the incorporation of VTET, which has a dark brown colour, the colour of the topcoat becomes slightly brownish as shown in Figure 4.1.

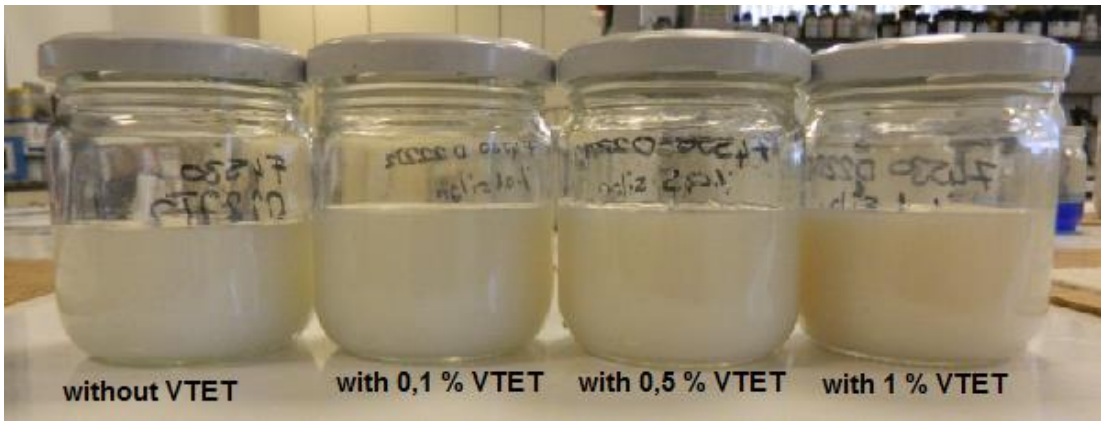


Figure 4.1 : Colour of VTET incorporated topcoats.

Topcoats are applied on glass by an applicator with 100 µ wet film thickness as shown in Figure 4.2.

Figure 4.2 : Application by an applicator.

Wet films are shown in Figure 4.3.

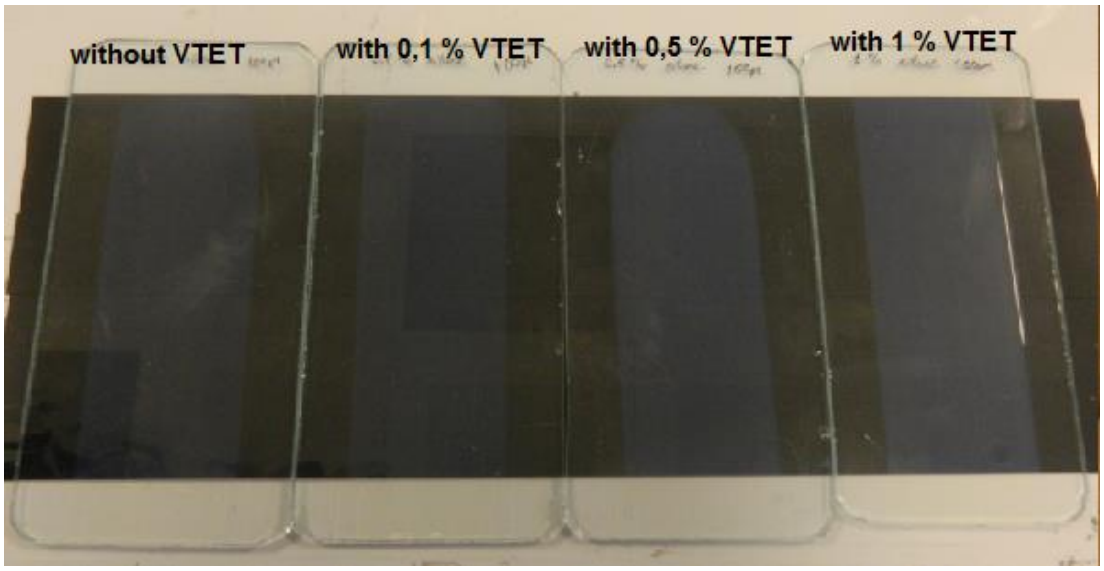


Figure 4.3 : Wet films of topcoats on glass.

Dried films on glass are shown in Figure 4.4.

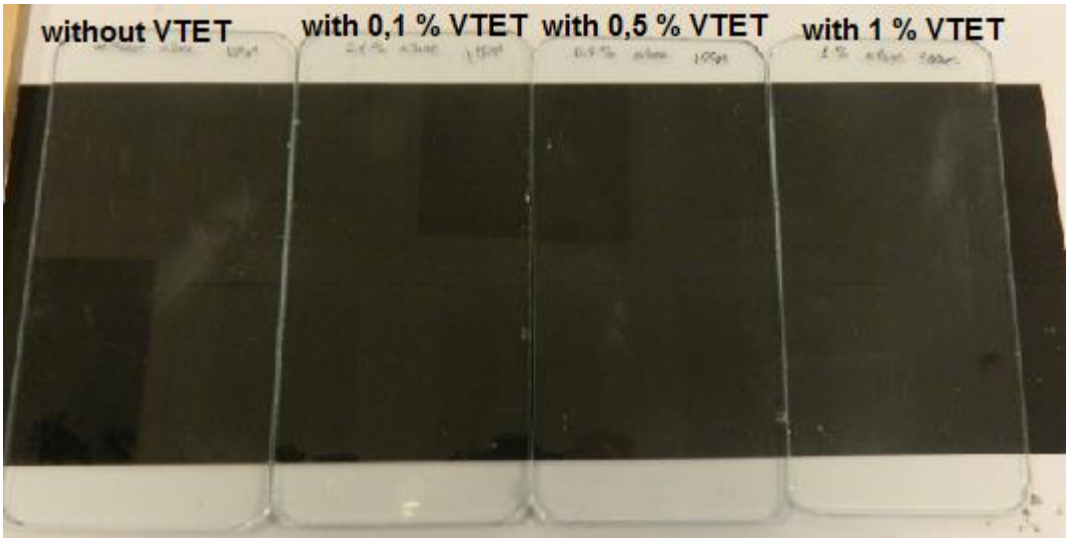


Figure 4.4 : Dried films of topcoats on glass.

Topcoats are also applied on beech veneer wood panel by spray application with 200 µ wet film thickness as shown in Figure 4.5.

Figure 4.5 : Topcoats applied on wood.

4.3.2 Effect on gloss

For gloss testing, clear topcoats are applied on a beech veneer wood panel where the wet film thickness is 200 µ. After 7 days curing, gloss at 20°, 60° and 85° are measured with Novo-Gloss Trio Statistical Glossmeter.

However increase in gloss is expected with the addition of VTET, gloss results on wood can not be correlated with the increasing amount of VTET. Results are given in Table 4.10.

Table 4.10 : Gloss results of applied topcoats on beech veneer panels.

Topcoat #	VTET %	Gloss 20° / 60° / 85°
Topcoat 1	0	6,9 / 29,3 / 25,4
Topcoat 2	0,1	5,5 / 18,5 / 11,6
Topcoat 3	0,5	7,6 / 25,8 / 21
Topcoat 4	1	5,2 / 19,7 / 13,9

4.3.3 Effect on adhesion

Effect on adhesion is tested by cross-cut pull off test method. There is no significant difference between topcoats. Figure 4.6 and Figure 4.7 shows cross-cut test on beech veneer wood panel.

Figure 4.6 : Cross-cut test.

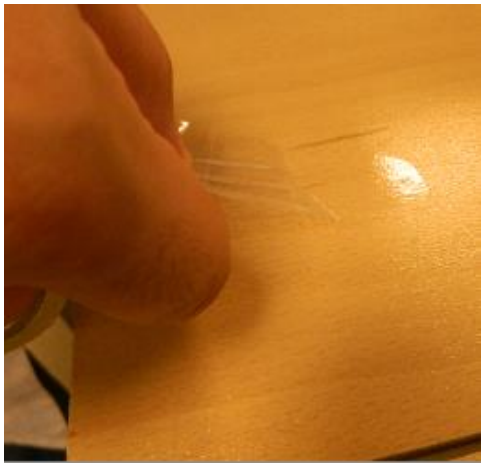


Figure 4.7 : Cross-cut test.

4.3.4 Effect on hydrophobicity

It is observed that with the increased amount of addition of VTET, hyrophobicity of the clear wood topcoat is increased as shown in Figure 4.8.

Figure 4.8 : Effect of VTET on hydrophobicity.

6. CONCLUSION

The aim of this study is to examine how a range of different anionic surfactants affect the polymerization of styrene-acrylic emulsion and the end properties of an interior clear wood coating system prepared with these copolymers.

The surfactants used in this study include different types of anionic surfactants as sodium lauryl suphate, sodium lauryl ether sulphate (2EO and 4EO), sodıum dodecylbenzene sulphonate, alkyl polyethylene glycol ether sulphate, polyoxyhethylene tridceyl phospate ester and disodium exthoxylated alcohol [C_{10}-C_{12}] half ester of sulfosuccinic acid.

For the sake of uniform conditions, the same recipe is used for polymerization except surfactant. Seven latexes were prepared as binders for interior clear wood coating. Particle size distribution of the copolymers are measured to check the effect of anionic surfactants.

Seven clear wood topcoat formulation prepared with the same fomulation except copolymer as the binder. Formed films prepared were tested for gloss, hardness, coin resistance, chemical resistance and blocking. The best performing topcoat formulation is selected and the sulphur containing silane VTET added in three different ratio as 0,1 %, 0,5 % and 1 %. The effect of VTET is also tested in terms of gloss, hardness, coin resistance, blocking nd hydropbohic character of the film.

Particle size results shows that sodium lauryl sulphate, sodium lauryl ether sulphate 2EO and sodium lauryl ether sulphate 4EO give similar particle size around 75 nm.

Alkyl polyethylene glycol ether sulphate and polyoxyethylene tridecyl phosphate ester gives biggest particle size within the surfactants around 105 nm.

In clear interior furniture topcoat formulation, the copolymer synthesized with sodium lauryl sulphate 4EO, performes as the best in terms of early blocking resistance which is one of the most important criterias in industrial interior wood coating process.

With the incorporation of VTET, sulphur-containing silane, hydrophobicity of the dried film increased.

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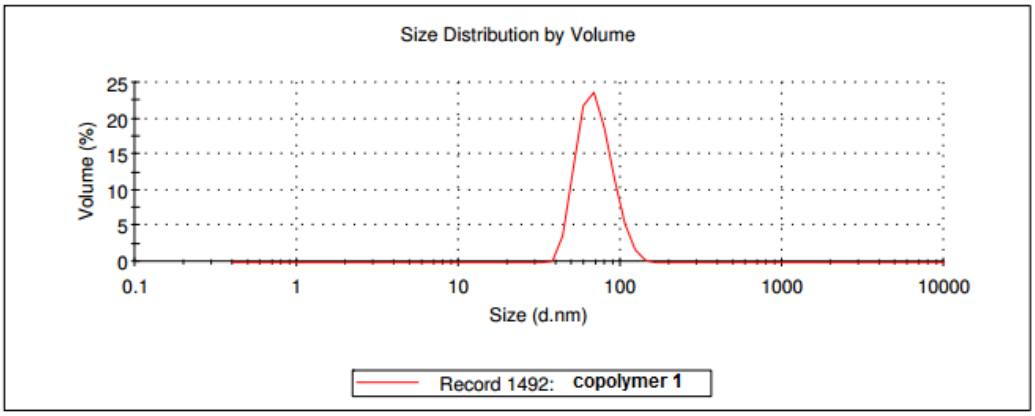
APPENDICES

APPENDIX A: Avarege particle size of copolymers (d.nm)

APPENDIX A

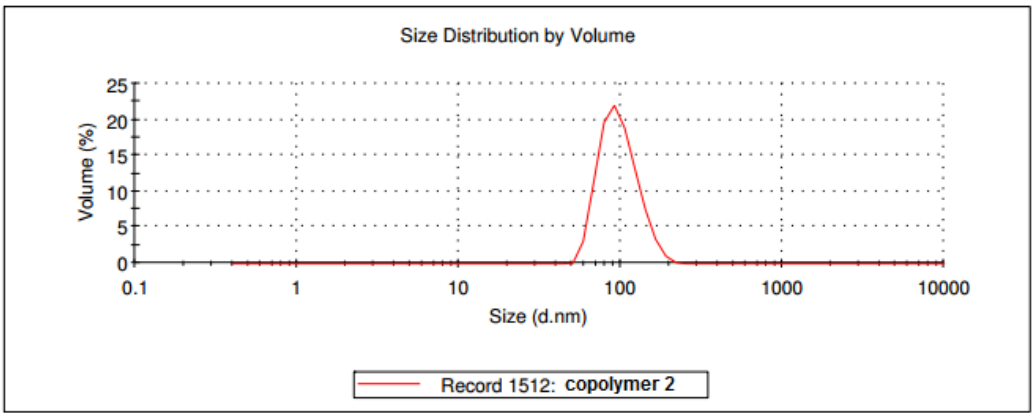


Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	76,56	**Peak 1:**	70,83	100,0	17,51
PdI:	0,014	**Peak 2:**	0,000	0,0	0,000
	0,958	**Peak 3:**	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	18,8	1106	0,0
0,4632	0,0	6,503	0,0	91,28	11,6	1281	0,0
0,5365	0,0	7,531	0,0	105,7	5,4	1484	0,0
0,6213	0,0	8,721	0,0	122,4	1,8	1718	0,0
0,7195	0,0	10,10	0,0	141,8	0,3	1990	0,0
0,8332	0,0	11,70	0,0	164,2	0,0	2305	0,0
0,9649	0,0	13,54	0,0	190,1	0,0	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,0	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,2	531,2	0,0	7456	0,0
3,122	0,0	43,82	3,7	615,1	0,0	8635	0,0
3,615	0,0	50,75	12,9	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	21,8	825,0	0,0		
4,849	0,0	68,06	23,6	955,4	0,0		

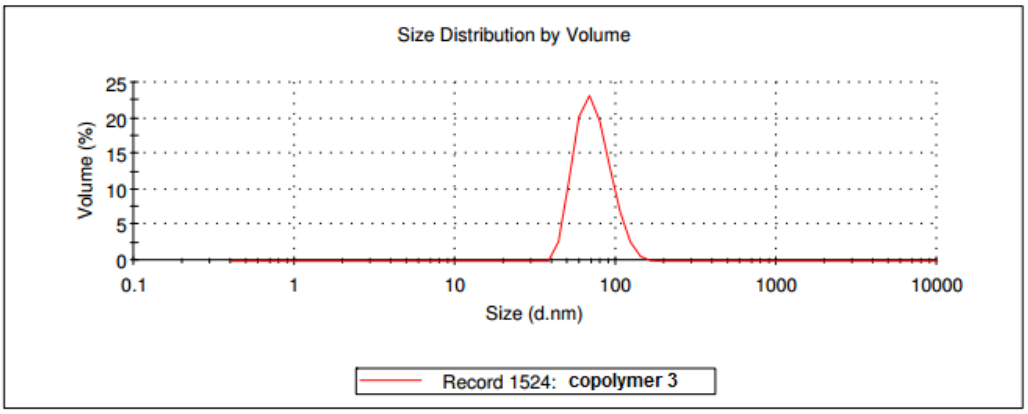


Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	104,9	Peak 1:	99,53	100,0	26,97
PdI:	0,041	Peak 2:	0,000	0,0	0,000
	0,946	Peak 3:	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	19,5	1106	0,0
0,4632	0,0	6,503	0,0	91,28	21,9	1281	0,0
0,5365	0,0	7,531	0,0	105,7	18,8	1484	0,0
0,6213	0,0	8,721	0,0	122,4	13,1	1718	0,0
0,7195	0,0	10,10	0,0	141,8	7,6	1990	0,0
0,8332	0,0	11,70	0,0	164,2	3,4	2305	0,0
0,9649	0,0	13,54	0,0	190,1	1,1	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,2	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,0	531,2	0,0	7456	0,0
3,122	0,0	43,82	0,0	615,1	0,0	8635	0,0
3,615	0,0	50,75	0,1	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	3,1	825,0	0,0		
4,849	0,0	68,06	11,3	955,4	0,0		

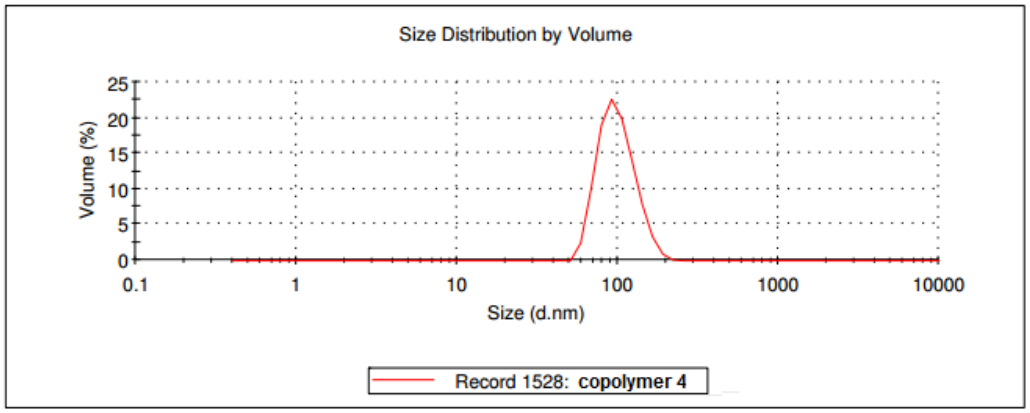


Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	79,47	Peak 1:	73,38	100,0	18,77
PdI:	0,021	Peak 2:	0,000	0,0	0,000
	0,953	Peak 3:	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	19,6	1106	0,0
0,4632	0,0	6,503	0,0	91,28	13,0	1281	0,0
0,5365	0,0	7,531	0,0	105,7	6,9	1484	0,0
0,6213	0,0	8,721	0,0	122,4	2,7	1718	0,0
0,7195	0,0	10,10	0,0	141,8	0,7	1990	0,0
0,8332	0,0	11,70	0,0	164,2	0,1	2305	0,0
0,9649	0,0	13,54	0,0	190,1	0,0	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,0	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,0	531,2	0,0	7456	0,0
3,122	0,0	43,82	2,7	615,1	0,0	8635	0,0
3,615	0,0	50,75	11,1	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	20,1	825,0	0,0		
4,849	0,0	68,06	23,1	955,4	0,0		

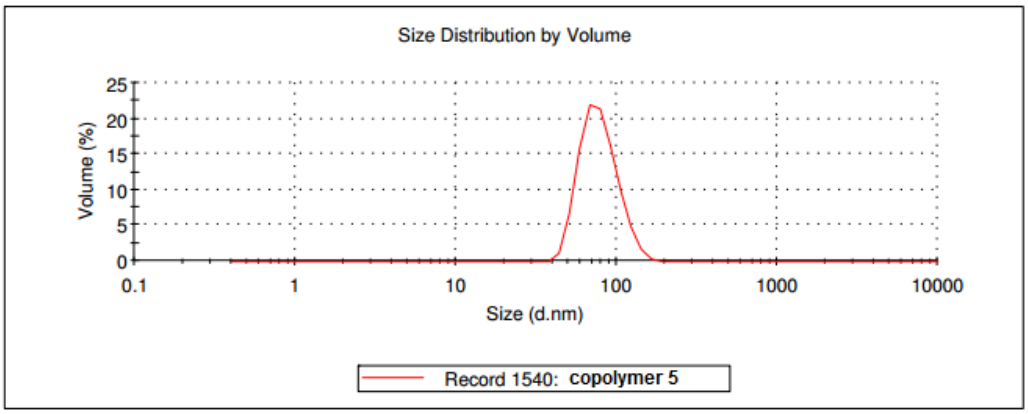


Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	105,7	Peak 1:	100,5	100,0	26,29
PdI:	0,030	Peak 2:	0,000	0,0	0,000
	0,951	Peak 3:	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	18,9	1106	0,0
0,4632	0,0	6,503	0,0	91,28	22,5	1281	0,0
0,5365	0,0	7,531	0,0	105,7	19,8	1484	0,0
0,6213	0,0	8,721	0,0	122,4	13,9	1718	0,0
0,7195	0,0	10,10	0,0	141,8	7,9	1990	0,0
0,8332	0,0	11,70	0,0	164,2	3,4	2305	0,0
0,9649	0,0	13,54	0,0	190,1	0,9	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,1	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,0	531,2	0,0	7456	0,0
3,122	0,0	43,82	0,0	615,1	0,0	8635	0,0
3,615	0,0	50,75	0,0	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	2,4	825,0	0,0		
4,849	0,0	68,06	10,1	955,4	0,0		

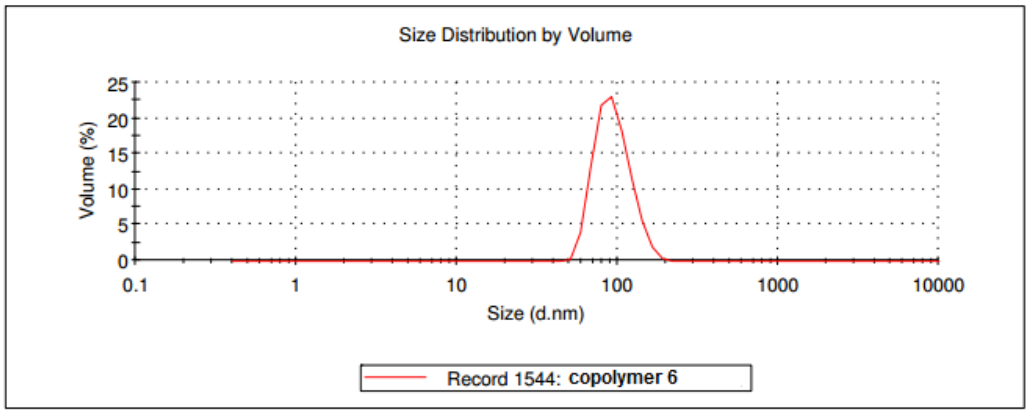


Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	85,89	Peak 1:	79,29	100,0	21,14
PdI:	0,029	Peak 2:	0,000	0,0	0,000
	0,949	Peak 3:	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	21,3	1106	0,0
0,4632	0,0	6,503	0,0	91,28	16,2	1281	0,0
0,5365	0,0	7,531	0,0	105,7	9,9	1484	0,0
0,6213	0,0	8,721	0,0	122,4	4,9	1718	0,0
0,7195	0,0	10,10	0,0	141,8	1,8	1990	0,0
0,8332	0,0	11,70	0,0	164,2	0,4	2305	0,0
0,9649	0,0	13,54	0,0	190,1	0,0	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,0	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,0	531,2	0,0	7456	0,0
3,122	0,0	43,82	1,2	615,1	0,0	8635	0,0
3,615	0,0	50,75	6,7	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	15,8	825,0	0,0		
4,849	0,0	68,06	21,9	955,4	0,0		

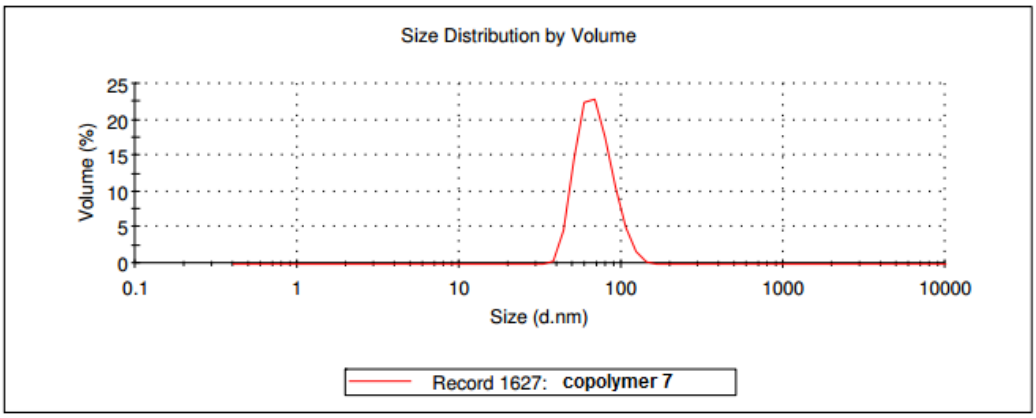


Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	100,5	Peak 1:	94,95	100,0	23,92
PdI:	0,013	Peak 2:	0,000	0,0	0,000
	0,956	Peak 3:	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	21,7	1106	0,0
0,4632	0,0	6,503	0,0	91,28	22,9	1281	0,0
0,5365	0,0	7,531	0,0	105,7	18,2	1484	0,0
0,6213	0,0	8,721	0,0	122,4	11,5	1718	0,0
0,7195	0,0	10,10	0,0	141,8	5,7	1990	0,0
0,8332	0,0	11,70	0,0	164,2	2,0	2305	0,0
0,9649	0,0	13,54	0,0	190,1	0,4	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,0	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,0	531,2	0,0	7456	0,0
3,122	0,0	43,82	0,0	615,1	0,0	8635	0,0
3,615	0,0	50,75	0,2	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	4,0	825,0	0,0		
4,849	0,0	68,06	13,4	955,4	0,0		



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	75,64	Peak 1:	69,72	100,0	17,65
PdI:	0,019	Peak 2:	0,000	0,0	0,000
	0,953	Peak 3:	0,000	0,0	0,000

Result quality Good

Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %	Size d.nm	Volume %
0,4000	0,0	5,615	0,0	78,82	17,5	1106	0,0
0,4632	0,0	6,503	0,0	91,28	10,7	1281	0,0
0,5365	0,0	7,531	0,0	105,7	5,1	1484	0,0
0,6213	0,0	8,721	0,0	122,4	1,7	1718	0,0
0,7195	0,0	10,10	0,0	141,8	0,3	1990	0,0
0,8332	0,0	11,70	0,0	164,2	0,0	2305	0,0
0,9649	0,0	13,54	0,0	190,1	0,0	2669	0,0
1,117	0,0	15,69	0,0	220,2	0,0	3091	0,0
1,294	0,0	18,17	0,0	255,0	0,0	3580	0,0
1,499	0,0	21,04	0,0	295,3	0,0	4145	0,0
1,736	0,0	24,36	0,0	342,0	0,0	4801	0,0
2,010	0,0	28,21	0,0	396,1	0,0	5560	0,0
2,328	0,0	32,67	0,0	458,7	0,0	6439	0,0
2,696	0,0	37,84	0,4	531,2	0,0	7456	0,0
3,122	0,0	43,82	4,7	615,1	0,0	8635	0,0
3,615	0,0	50,75	14,4	712,4	0,0	1,000e4	0,0
4,187	0,0	58,77	22,4	825,0	0,0		
4,849	0,0	68,06	22,8	955,4	0,0		

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